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## Seasonality and spatial heterogeneity of the surface ocean carbonate system in the northwest European continental shelf

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## ABSTRACT

In 2014–5 the UK NERC sponsored an 18 month long Shelf Sea Biogeochemistry research programme which collected over 1500 nutrient and carbonate system samples across the NW European Continental shelf, one of the largest continental shelves on the planet. This involved the cooperation of 10 different Institutes and Universities, using 6 different vessels. Additional carbon dioxide (CO<sub>2</sub>) data were obtained from the underway systems on three of the research vessels. Here, we present and discuss these data across 9 ecohydrodynamic regions, adapted from those used by the EU Marine Strategy Framework Directive (MSFD). We observed strong seasonal and regional variability in carbonate chemistry around the shelf in relation to nutrient biogeochemistry. Whilst salinity increased (and alkalinity decreased) out from the near-shore coastal waters offshore throughout the year nutrient concentrations varied with season. Spatial and seasonal variations in the ratio of DIC to nitrate concentration were seen that could impact carbon cycling. A decrease in nutrient concentrations and a pronounced under-saturation of surface pCO<sub>2</sub> was evident in the spring in most regions, especially in the Celtic Sea. This decrease was less pronounced in Liverpool Bay and to the North of Scotland, where nutrient concentrations remained measurable throughout the year. The near-shore and relatively shallow ecosystems such as the eastern English Channel and southern North Sea were associated with a thermally driven increase in pCO<sub>2</sub> to above atmospheric levels in summer and an associated decrease in pH. Non-thermal processes (such as mixing and the remineralisation of organic material) dominated in winter in most regions but especially in the northwest of Scotland and in Liverpool Bay. The large database collected will improve understanding of carbonate chemistry over the North-Western European Shelf in relation to nutrient biogeochemistry, particularly in the context of climate change and ocean acidification.

### 1. Introduction

Continental shelf seas are important net sinks of atmospheric CO<sub>2</sub>, occupying only 7% of the global sea surface area (Chen and Borges, 2009). However, there are considerable uncertainties in the contributions of individual shelf seas to regional (and global) carbon budgets

(Borges, 2005). Continental shelves have high levels of biological activity due to cross shelf and riverine nutrient supply, and to rapid organic matter recycling from the close pelagic-benthic coupling on the shelf (Liu et al., 2010). The seawater partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) is controlled by seasonal changes in temperature and phytoplankton productivity (Zeebe and Wolf-Gladrow, 2001). Additional factors such

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as coccolithophore calcification (Harley et al., 2010) can influence seasonal variations in seawater  $p\text{CO}_2$ .

The northeast Atlantic continental shelf is a net  $\text{CO}_2$  sink, of about  $-17 \text{ Tg C yr}^{-1}$  (compared with the global estimated shelf sink of  $-0.2 \text{ Pg C yr}^{-1}$ ; Laruelle et al., 2014) and thus significant on both a regional and global basis as a hotspot of  $\text{CO}_2$  uptake. It comprises both well-mixed and stratified regions, which have different capacities to take up  $\text{CO}_2$ . Generally the well mixed near-shore heterotrophic ecosystems act as sources of  $\text{CO}_2$  to the atmosphere and the seasonally stratified autotrophic continental shelf systems act as sinks of atmospheric  $\text{CO}_2$  (Borges, 2005; Chen and Borges, 2009). An example of the former is the southern North Sea (Thomas et al., 2004) and the south western English Channel (Borges, 2005; Marrec et al., 2013, 2015). An example of the latter is the seasonally stratified northern North Sea, which is an order of magnitude stronger  $\text{CO}_2$  sink than the well-mixed eastern English Channel (Thomas et al., 2004, 2007). In the boundary between the off-shelf and on-shelf waters, a continuous injection of nutrients can arise due to processes such as internal tides, internal waves, eddies and slope current mixing, which can enhance productivity (Pingree, 1975; Garcia-Soto and Pingree, 1998) and the potential  $\text{CO}_2$  sink.

Monitoring the seawater total alkalinity (TA) and dissolved inorganic carbon (DIC), along with its  $p\text{CO}_2$ , will help describe the oceanic carbonate system. The exact definition of TA is complicated but it can be summarised as the stoichiometric sum of bases in solution (Wolf-Gladrow et al., 2007). Many processes can influence TA such as benthic calcification and dissolution, the growth of coccolithophore blooms (Harley et al., 2010); the contribution of organic matter (Koeve et al., 2012; Hoppe et al., 2012); changes in riverine input (Hydes and Hartman, 2012) and nitrate uptake (Brewer and Goldman, 1976).

The anthropogenic increase in atmospheric  $\text{CO}_2$  and uptake by seawater is driving a decline in oceanic pH known as ocean acidification (OA) (Caldeira and Wickett, 2003; Doney et al., 2009; Gattuso and Hansson, 2011). It is also important to measure nutrient concentrations as an indication of potential primary production, as this will influence  $p\text{CO}_2$  (and therefore seawater pH) through the balance between photosynthesis and respiration.

The general features of the annual cycle of nutrient and plankton concentrations on the northwest European shelf have been established for some time (Cushing, 1973; Johnston, 1973; Gerlach, 1988; Nelissen and Stefels, 1988). Within the North Sea, the NERC North Sea Programme in 1988–89, provided the first data set with sufficient information to allow seasonal changes in nutrient concentrations and plankton biomass to be investigated quantitatively (Howarth et al., 1996). Seasonal variation in carbonate chemistry has also been followed at time series sites (eg: the L4 and Stonehaven sites during the 2008–2010 DEFRApH project, Hydes et al., 2011) or through surveys around the NW European shelf (e.g. Thomas et al., 2004, which was based on 4 surveys of the North Sea).

UK-SSB was established in 2014 to improve our understanding of carbon and nutrient cycling within shelf seas. As part of the ‘CANDY-FLOSS’ (Carbon and Nutrient Dynamics and Fluxes Over Shelf Systems) component of UK-SSB, sampling was carried out across the entire NW European continental shelf for DIC, TA and inorganic nutrients. The UK-SSB sampling campaign was a large marine research community effort that started in January 2014 and continued for eighteen months, involving the cooperation of 10 institutes and universities and 6 vessels. One aim of the present study was to increase the density and spatial coverage of carbon and nutrient sampling across the entire NW European shelf, using the shelf wide sampling component of the UK Shelf Sea Biogeochemistry research programme (UK-SSB, <http://www.uk-ssb.org/>). Our aim was to describe how the biogeochemical variables are distributed and interrelated on the shelf, both through the year and across 9 ecohydrodynamic regions, adapted from those used by the EU Marine Strategy Framework Directive (MSFD).

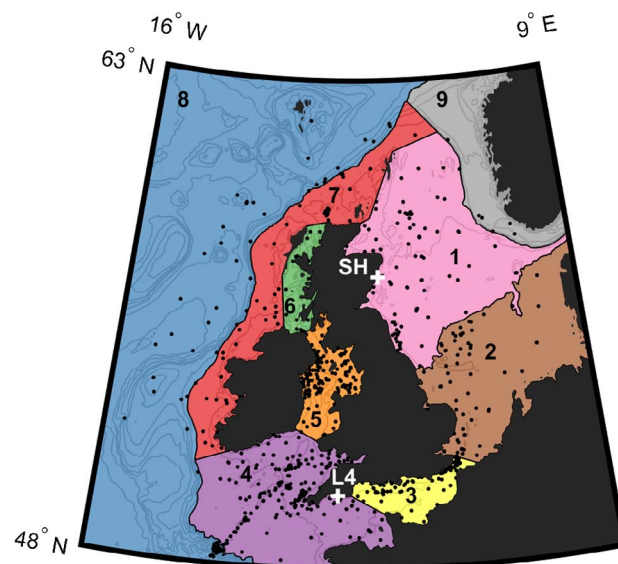


Fig. 1. Map of the sampling positions (black dots) during UK-SSB (2014–2015). Coloured areas 1–9 show the UK ecohydrodynamic regions used for MSFD reporting (adapted from Bresnan et al., 2015 to now include Ireland and the Norwegian Trench and showing the 200 m contour). White pluses show the time series sites SH (Stonehaven) and L4.

## 2. Materials and methods

### 2.1. Division of data into ecohydrodynamic regions

Ecohydrodynamic regions of the NW European Shelf are defined for reporting under the EU Marine Strategy Framework Directive (MSFD). The regions have been adapted from those defined in Charting Progress 2 (UKMMAS, 2010) and Bresnan et al., (2015), with the addition of the Irish Continental Shelf and the Norwegian Trench. They are distinguished by water depth (and seasonal stratification), proximity to the coast, riverine inputs (salinity) and water temperature ranges. These regions and the sampling positions are shown in Fig. 1.

Complex tidal fronts and topography separate the well-mixed and seasonally stratified waters across the shelf. This will strongly influence the biogeochemical dynamics of the area (as shown by Simpson and Hunter, 1974). The biogeochemical divide along the 50 m contour separates the seasonally stratified northern North Sea (region 1) from the shallower, well-mixed southern North Sea (region 2). The North Sea is influenced by the Atlantic Ocean to the North (Huthnance et al., 1997) and by riverine input, especially to the south (Hydes et al., 1999; Bresnan et al., 2015). The northern North Sea acts as a down-welling system (Huthnance et al., 2009). In the southern North Sea the entire water column remains well mixed throughout the year, likewise the eastern Channel (region 3) has shallow (0–100 m) and tidally well mixed waters. The deeper western Channel and Celtic Sea (region 4) has strong seasonal stratification with Atlantic influences in the Celtic Sea (Pingree, 1993; Simpson and Hunter, 1974). The relatively shallow and enclosed Irish Sea and especially Liverpool Bay (region 5) have a high influence of fresh water input (Hydes and Hartman, 2012; Greenwood et al., 2011).

Waters west of Scotland and the Minches (region 6) are made up of North Atlantic Ocean waters and form part of the continental shelf current but are modified by coastal influences (Bresnan et al., 2015). The Scottish and Irish continental shelf (region 7) are characterised by seasonal stratification and, as defined here, have a western limit of the 200 m depth contour. This region is influenced both by exchanges with the North Atlantic deep water and by water flowing from the south in the shelf edge current (Pingree, 1993; Huthnance, 1995, 1997; Hydes et al., 2004). The deep-sea waters beyond the 200 m contour are oceanic in origin and the Atlantic Approaches (region 8) encompasses

the Rockall Trough and the Faeroe/Shetland Channel. The Norwegian Trench (region 9) is the main outflow path for water leaving the North Sea, and it is permanently stratified (Van Leeuwen et al., 2015).

## 2.2. Sample collection

Between January 2014 and August 2015, multiple organisations collected samples from the underway water supply of their vessels on a daily basis whenever they were at sea around the NW European shelf (Fig. 1). Data were obtained from RRS *Discovery* (8 cruises), RRS *James Cook* (1 cruise), RV *Cefas Endeavour* (34 cruises), RV *Celtic Explorer* (6 cruises), RV *Scotia* (7 cruises), RV *Corys* (15 cruises), with additional samples from the fixed point monitoring sites Stonehaven in the North Sea and L4 in the English Channel (Fig. 1). All data are available from BODC <http://www.uk-ssb.org/data/> and as listed in the references from Humphreys et al. (2017a–h).

On approximately 1500 occasions, surface samples were collected from the underway seawater supply (nominal 5 m depth). For DIC and TA analysis the samples were collected into borosilicate glass bottles (preserved with 0.05 ml saturated mercuric chloride solution following Dickson et al., 2007), and the nutrient samples were filtered and frozen. At the time of sampling the temperature and salinity was recorded from the underway sensors. Additional near surface (0–20 m) samples were taken using a rosette sampler on the UK-SSB cruises in the Celtic Sea, on the RV *Cefas Endeavour* and on a supporting cruise to the Hebrides Shelf (Painter et al., 2016; Hartman et al., 2017).

## 2.3. Chemical analysis

DIC and TA were mostly (> 95%) measured using VINDTA 3C (Marianda, Germany) instruments in our shore based laboratory in Southampton. DIC analysis on the VINDTA involves reaction with 10% phosphoric acid, which converts DIC to CO<sub>2</sub> gas. This is carried by nitrogen into the coulometer cell where it reacts with monoethanolamine forming a titratable acid, which causes fading of the blue indicator. Responding to the colour change, an electrical current generates base to remove the acid and restore the indicator to the original colour. The amount of CO<sub>2</sub> can be estimated from the total current required (corrected for a blank), and DIC concentration can then be calculated given the sample volume. TA was measured by titration with hydrochloric acid (HCl ~ 0.10 mol l<sup>-1</sup>) using an open cell procedure, with a pH half-cell electrode (glass bodied Orion 8101SC, Ross, USA) and an Ag/AgCl reference electrode (model 6.0729.100, Metrohm, Switzerland). A modified Gran plot approach was used to calculate TA (Humphreys, 2015). Approximately 5% of the DIC and TA measurements were conducted using the Apollo SciTech (USA) DIC Analyzer (AS-C3) and Total Alkalinity Titrator (AS-ALK2). The AS-C3 functions similarly to the VINDTA 3C except that the final CO<sub>2</sub> measurement is by infrared absorbance (LI-COR). The AS-ALK2 performs a potentiometric titration with 0.1 M HCl to determine the TA.

In order to calibrate the results, seawater reference material (RM) obtained from A.G. Dickson (Scripps Institution of Oceanography, USA) were analysed each day (Dickson et al., 2003). Precision was assessed through repeated measurements of pooled seawater samples (n > 3) before each batch of sample analysis. The 1 $\sigma$  precision for the whole dataset was estimated as  $\pm 2.6 \mu\text{mol kg}^{-1}$  for DIC and  $\pm 2.7 \mu\text{mol kg}^{-1}$  for TA for VINDTA measurements. For the Apollo measurements, precision was estimated as  $\pm 4.0 \mu\text{mol kg}^{-1}$  and  $\pm 3.9 \mu\text{mol kg}^{-1}$  for DIC and TA respectively (Humphreys et al., 2018).

During the SSB shelf wide sampling, underway pCO<sub>2</sub> was measured on-board the RV *Cefas Endeavour* and on the NERC research vessel RRS *Discovery* using PML-Dartcom systems (Kitidis et al., 2012). Briefly, this comprises of a vented ‘showerhead’ equilibrator, Peltier cooler for partial drying of the equilibrated gas stream, non-dispersive infrared detection (Licor; LI-840) and associated mechanical/electronic hardware. The system was calibrated against three reference gases (BOC

Gases, UK; nominal concentrations 250, 380 and 450 ppmv CO<sub>2</sub> in synthetic air mixtures; changing from 450 ppm to 600 ppm on the RV *Cefas Endeavour* from November 2014) which were referenced against primary reference gases (National Oceanic and Atmospheric Administration, 244.9 and 444.4 ppm CO<sub>2</sub>). A recent at-sea inter-comparison with a similar but independent system, along with other carbonate observations, found the system was precise to within  $\pm 4 \mu\text{atm}$  (Ribas-Ribas et al., 2014). The atmospheric pCO<sub>2</sub> was calculated from monthly averaged pCO<sub>2</sub> measured at Mace Head (53.33°N, 9.90°W) (Humphreys et al., 2018).

Inorganic nutrients were analysed using a ‘Bran and Luebbe AA3’ segmented flow colorimetric nutrient auto-analyser. The analytical methods were phosphate and silicate using Kirkwood (1989) and nitrate (plus nitrite) with Brewer and Riley (1965) methods. The standard deviation for duplicate measurements was within 2% and quality was assured through daily use of certified reference materials provided by KANSO (Japan). Sampling protocols and methodologies were carried out where possible according to the GO-SHIP nutrient analytical procedures manual (Hydes et al., 2010) including assessment of detection limits (eg:  $0.1 \mu\text{mol kg}^{-1}$  for nitrate).

## 2.4. Calculations

The carbonate system is characterised through knowing any two parameters out of TA, DIC, pCO<sub>2</sub> or pH and then using equilibrium equations and constants (Park, 1969) and the CO<sub>2</sub>SYS program (Lewis et al., 1998) to calculate the remaining parameters. The shelf wide UK-SSB measurements of DIC, TA temperature, salinity and nutrient data, were used to calculate pH (free scale, as recommended by Waters and Millero, 2013), pCO<sub>2</sub>, calcite ( $\Omega_c$ ) and aragonite ( $\Omega_a$ ) saturation using the CO<sub>2</sub>SYS program (Lewis et al., 1998) with the Mehrbach constants (according to Dickson and Millero, 1987). Known uncertainties associated with calculations in CO<sub>2</sub>SYS using bottle DIC and TA results as inputs lead to an uncertainty of  $\pm 6 \mu\text{atm}$  in the calculation of pCO<sub>2</sub> (eg: Millero et al., 2002). These arise from inaccuracies in the measurements and in the determination of dissociation constants. Calculated pCO<sub>2</sub> values were checked against direct measurements of pCO<sub>2</sub> measured by underway systems on 60 occasions on-board the RV *Cefas Endeavour* and RRS *Discovery* research vessels. The average difference was  $2 \mu\text{atm}$  with a variation of up to  $\pm 27 \mu\text{atm}$  between the calculated and measured pCO<sub>2</sub>. We calculated pH from DIC and TA, despite this pair not being ideal for this purpose (errors will be  $\pm 0.006$ ; Millero et al., 2002), in order to give a general picture of seasonal and regional variations in pH on the shelf.

The thermal and non-thermal components of pCO<sub>2</sub> were calculated by assessing the change in pCO<sub>2</sub> relative to the average of all winter data in the survey, the winter mean state ( $386 \mu\text{atm}$ ), then calculating the thermal component at the mean winter temperature (9.1 °C) following Takahashi et al. (2002). The residual between the total and thermal component of change was calculated to assess the non-thermal, or largely biological, component.

## 3. Results

All results are presented with January to March defined as winter, April–June as spring, July–September as summer and October–December as autumn when describing the seasonal distribution in biogeochemical variables. Table 1 shows the seasonal mean average (and standard deviation) for each variable and region. As the sampling was not distributed evenly in space and time some regions remain under-sampled, especially the Minches (region 6) in autumn and in the Norwegian Trench (region 9), as indicated in Table 1.

### 3.1. Hydrographic variability

Fig. 2 shows the seasonal variation in sea surface temperature (SST)

**Table 1a**  
The mean average (and standard deviation) for the hydrograph and nutrient data in winter (jan-mar), spring (apr-jun), summer (jul-sep) and autumn (oct-dec) for each of the 9 ecohydrographic regions (numbered 1–9). Where insufficient samples exist, n/a has been used.

	Temperature (°C)				Practical salinity				Phosphate ( $\mu\text{mol kg}^{-1}$ )				Silicate ( $\mu\text{mol kg}^{-1}$ )				Nitrite ( $\mu\text{mol kg}^{-1}$ )			
	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec
1	7.65 (0.52)	13.78 (2.44)	14.36 (1.27)	11.65 (0.45)	33.26 (3.9)	34.11 (0.40)	34.61 (0.61)	34.78 (0.02)	0.54 (0.08)	0.08 (0.11)	0.09 (0.08)	0.36 (0.01)	3.59 (1.55)	0.95 (0.57)	0.75 (0.60)	3.07 (0.49)	0.12 (0.08)	0.03 (0.07)	0.06 (0.10)	0.18 (0.01)
2	7.86 (0.85)	12.40 (1.27)	17.69 (1.67)	14.24 (1.28)	34.08 (1.53)	34.56 (0.36)	34.43 (0.42)	34.67 (0.34)	0.35 (0.12)	0.10 (0.07)	0.16 (0.13)	0.50 (0.12)	2.13 (1.48)	0.80 (0.53)	1.92 (1.77)	3.72 (2.13)	0.14 (0.10)	0.02 (0.05)	0.10 (0.15)	0.59 (0.46)
3	9.44 (0.70)	12.25 (1.93)	18.27 (0.80)	16.69 (1.25)	34.95 (0.54)	30.64 (10.81)	34.86 (0.29)	35.15 (0.11)	0.53 (0.05)	0.08 (0.07)	1.91 (6.46)	0.35 (0.26)	5.10 (2.33)	2.88 (9.18)	3.62 (5.72)	3.76 (1.44)	0.10 (0.06)	0.11 (0.25)	0.09 (0.13)	0.19 (0.14)
4	9.48 (0.57)	11.32 (1.56)	16.63 (2.68)	15.84 (5.89)	35.22 (0.14)	35.27 (0.17)	34.12 (4.42)	33.39 (6.43)	0.53 (0.12)	0.21 (0.16)	0.09 (0.16)	0.27 (0.23)	4.23 (0.90)	2.14 (0.93)	0.80 (1.17)	2.27 (1.62)	0.10 (0.08)	0.07 (0.05)	0.08 (0.29)	0.23 (0.17)
5	8.00 (1.40)	10.53 (1.84)	15.37 (1.14)	14.06 (0.89)	33.80 (0.78)	33.81 (0.81)	34.02 (0.46)	34.19 (0.36)	0.64 (0.22)	0.36 (0.21)	0.25 (0.18)	0.95 (2.15)	7.54 (3.34)	3.00 (2.30)	2.13 (1.19)	5.31 (5.59)	0.13 (0.18)	0.11 (0.09)	0.15 (0.23)	0.23 (0.36)
6	9.35 (0.39)	12.14 (0.73)	12.47 (0.35)	n/a	34.45 (0.09)	34.00 (0.35)	34.24 (0.16)	n/a	0.53 (0.02)	0.19 (0.12)	0.24 (0.03)	0.19 (0.03)	4.53 (0.32)	1.29 (0.78)	1.43 (0.39)	n/a	0.06 (0.01)	0.10 (0.07)	0.25 (0.18)	n/a
7	8.74 (0.58)	9.70 (1.80)	14.01 (1.05)	18.41 (0.87)	34.53 (0.50)	34.94 (0.42)	35.11 (0.27)	34.87 (0.2)	0.59 (0.04)	0.42 (0.27)	0.13 (0.11)	0.36 (0.03)	4.56 (1.01)	1.54 (0.79)	0.48 (0.29)	2.65 (0.43)	0.27 (0.13)	0.23 (0.14)	0.06 (0.05)	0.31 (0.18)
8	9.88 (0.15)	11.31 (1.49)	16.16 (1.69)	14.12 (0.39)	35.39 (0.04)	35.65 (0.99)	35.54 (0.15)	35.58 (0.00)	0.62 (n/a)	0.43 (0.18)	0.10 (0.07)	n/a	3.30 (n/a)	2.25 (1.39)	0.36 (0.17)	n/a	0.07 (n/a)	0.17 (0.06)	0.04 (0.05)	n/a
9	n/a	10.75 (1.91)	14.03 (0.80)	n/a	n/a	34.26 (0.61)	34.65 (0.43)	n/a	n/a	0.17 (0.14)	0.04 (0.02)	n/a	n/a	1.29 (0.56)	0.42 (0.29)	n/a	n/a	0.16 (0.26)	0.01 (n/a)	n/a

**Table 1b**  
The mean average (and standard deviation) for nitrate and carbonate data in winter (jan-mar), spring (apr-jun), summer (jul-sep) and autumn (oct-dec) for each of the 9 ecohydrographic regions (numbered 1–9). Where insufficient samples exist, n/a has been used.

	Nitrate ( $\mu\text{mol kg}^{-1}$ )				DIC ( $\mu\text{mol kg}^{-1}$ )				TA ( $\mu\text{mol kg}^{-1}$ )				pH				pCO <sub>2</sub> ( $\mu\text{atm}$ )			
	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec
1	7.40 (1.52)	0.51 (1.42)	0.33 (0.56)	5.42 (0.01)	2133.27 (23.38)	2033.72 (31.65)	2063.51 (17.24)	2110.95 (0.45)	2309.71 (29.42)	2275.17 (28.38)	2291.11 (19.02)	2294.62 (7.21)	8.18 (0.15)	8.19 (0.06)	8.15 (0.04)	8.09 (0.01)	351.51 (81.80)	331.07 (52.03)	362.89 (73.54)	427.85 (8.78)
2	4.60 (3.22)	1.11 (2.70)	0.66 (1.06)	6.10 (7.39)	2147.12 (44.05)	2097.67 (18.89)	2110.98 (37.72)	2144.89 (24.54)	2319.90 (31.15)	2314.85 (29.59)	2316.10 (42.68)	2331.90 (32.12)	8.12 (0.03)	8.15 (0.07)	8.05 (0.10)	8.06 (0.01)	382.05 (31.20)	376.22 (58.66)	483.40 (79.58)	469.14 (11.83)
3	9.56 (3.51)	4.13 (10.42)	3.77 (9.91)	3.45 (3.24)	2133.52 (8.08)	2102.09 (36.38)	2089.84 (14.69)	2102.80 (10.39)	2326.21 (14.26)	2341.57 (26.17)	2316.24 (12.97)	2323.77 (10.25)	8.13 (0.02)	8.19 (0.06)	8.09 (0.02)	8.10 (0.04)	377.89 (19.73)	333.08 (54.69)	452.43 (29.21)	436.64 (48.60)
4	6.55 (3.69)	2.05 (2.44)	0.49 (2.28)	3.37 (4.06)	2140.49 (7.93)	2111.78 (23.78)	2086.91 (18.09)	2116.19 (21.57)	2332.68 (9.60)	2333.32 (10.09)	2335.20 (14.97)	2337.16 (16.05)	8.12 (0.01)	8.17 (0.03)	8.14 (0.04)	8.12 (0.04)	388.10 (13.26)	354.57 (49.11)	389.88 (49.11)	405.53 (44.77)
5	9.86 (6.09)	3.94 (3.86)	1.03 (1.25)	5.27 (4.54)	2143.20 (18.26)	2095.01 (52.36)	2076.72 (25.23)	2110.78 (12.83)	2298.23 (26.64)	2294.04 (30.14)	2293.79 (12.89)	2305.37 (10.68)	8.07 (0.04)	8.14 (0.10)	8.12 (0.05)	8.08 (0.03)	435.29 (40.78)	364.82 (62.10)	409.35 (54.79)	446.75 (28.48)
6	6.31 (0.99)	0.99 (1.50)	1.94 (1.07)	0.00 (0.00)	2129.04 (15.18)	2065.03 (30.84)	2090.22 (7.20)	n/a	2287.09 (10.89)	2294.17 (10.11)	2286.60 (7.31)	n/a	8.06 (0.05)	8.18 (0.05)	8.11 (0.03)	n/a	452.97 (62.04)	333.27 (43.92)	402.89 (27.48)	n/a
7	7.88 (3.37)	5.53 (4.11)	1.21 (1.27)	4.91 (0.64)	2117.70 (47.20)	2112.53 (30.49)	2090.19 (15.82)	2127.98 (27.17)	2320.55 (31.78)	2323.43 (14.33)	2301.07 (8.49)	2316.16 (26.90)	8.16 (0.05)	8.17 (0.04)	8.11 (0.04)	8.10 (0.02)	347.37 (51.67)	342.94 (29.78)	411.17 (41.43)	418.57 (19.97)
8	10.23 (n/a)	6.71 (2.99)	0.59 (1.00)	n/a	2138.65 (2.94)	2129.34 (16.17)	2089.56 (11.36)	n/a	2332.34 (8.47)	2335.43 (6.30)	2329.87 (17.18)	n/a	8.12 (n/a)	8.15 (0.03)	8.15 (0.03)	n/a	386.80 (n/a)	372.79 (24.80)	372.79 (32.84)	n/a
9	n/a	0.67 (0.91)	0.14 (n/a)	n/a	n/a	2070.94 (0.13)	2060.83 (12.05)	n/a	n/a	2298.60 (35.53)	2294.63 (0.06)	n/a	n/a	8.19 (0.03)	8.16 (0.04)	n/a	n/a	325.05 (12.54)	355.18 (38.98)	n/a



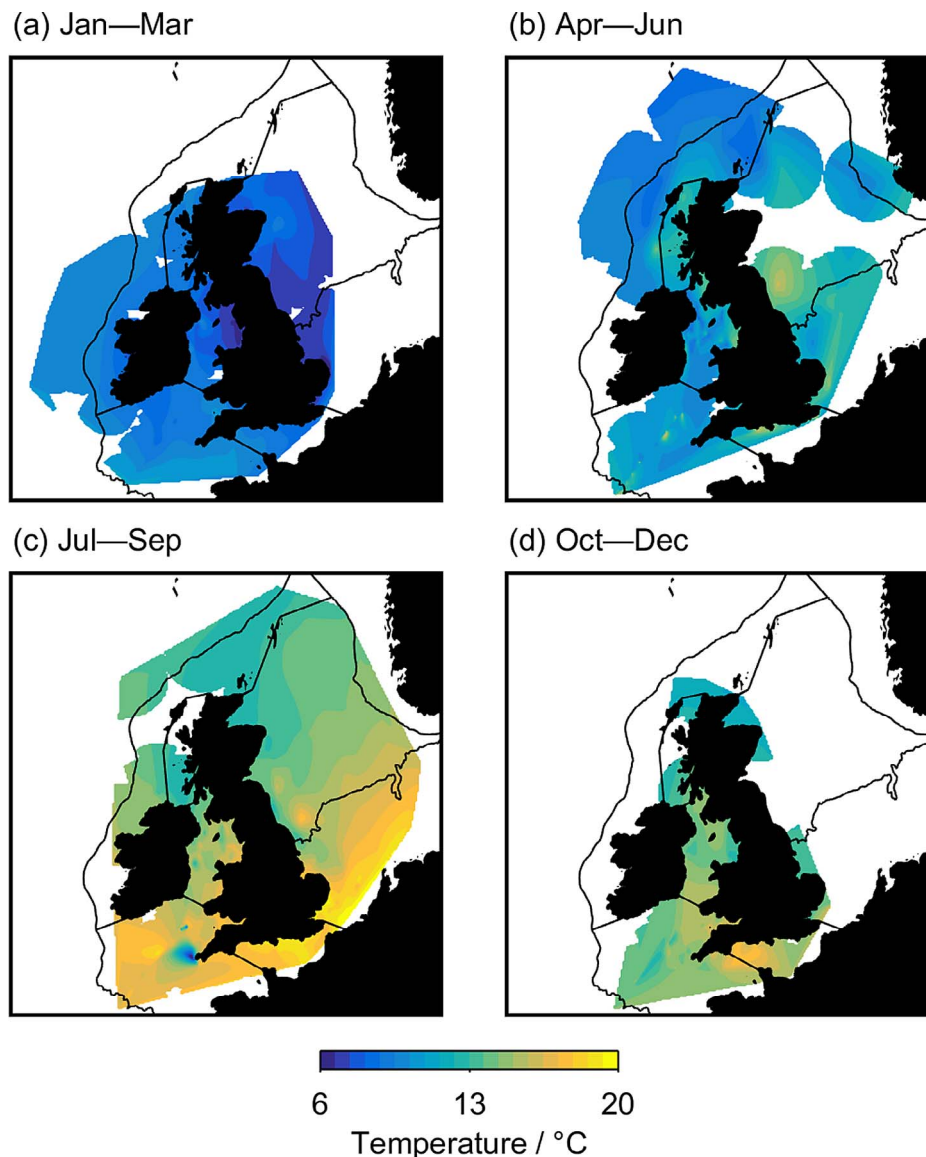


Fig. 2. Seasonal maps of sea surface temperature (SST), using sensor data taken at the point of sampling on the SSB surveys. Figs. 2–9, 12–15 are all mapped from 48 to 62°N, 16°W to 8°E showing winter (Jan–Mar), spring (Apr–Jun), summer (Jul–Sep) and autumn (Oct–Dec).

around an average of 14 °C. The coldest surface waters (average 7.65 °C) were seen in winter, especially in the North Sea (region 1, Table 1a). The warmest surface waters were generally observed to the south and in the summer, (eg: average of 18.27 °C Eastern English Channel (region 3). Warm sea surface temperatures (16.69 °C), were still apparent in the autumn in the Eastern English Channel (region 3). Overall the regional variations were dominated by a decrease in SST to the north (Fig. 2).

Fig. 3 shows the seasonal and regional variation in sea surface salinity (SSS). Regional variation dominated over seasonal variability and the shelf waters were fresher than the oceanic waters. The mean SSS for the whole data set was 34.5 with higher salinities from oceanic influence observed to the west on the Atlantic northwest approaches (35.6, region 8). A tongue of high salinity water was observed in the northern North Sea (region 1). This feature was especially prominent in summer (Fig. 2, where the average SSS was 34.6, Table 1a), showing the influence of the advection of Atlantic water into this region.

### 3.2. Chemical variability

#### 3.2.1. Nutrients

Figs. 4 and 5 show the seasonal and regional variation in surface inorganic nutrients. Generally nitrate concentrations were relatively high offshore, in the Atlantic waters off shelf (region 7) compared to the inner shelf regions in all seasons. In contrast, the silicate concentrations were generally lower on the outer shelf compared with the inner shelf (see Figs. 4 and 5). For example to the west of Ireland (in region 7) the average nitrate concentration in winter was relatively high ( $7.9 \mu\text{mol kg}^{-1}$ ) when the silicate concentrations were relatively low ( $4.6 \mu\text{mol kg}^{-1}$ ) as shown in Table 1.

Seasonally the highest nitrate and silicate concentrations were observed in winter, in all regions (Figs. 4 and 5). For example, the winter nutrient concentrations were high in the Irish Sea (region 5) with average winter nitrate and silicate of  $9.9 \mu\text{mol kg}^{-1}$  and  $7.5 \mu\text{mol kg}^{-1}$  respectively. However, relatively low nitrate concentrations ( $6.3 \mu\text{mol kg}^{-1}$ ) were observed in winter off the Scottish west coast (region 6).

In spring the lowest nitrate concentrations were observed in the

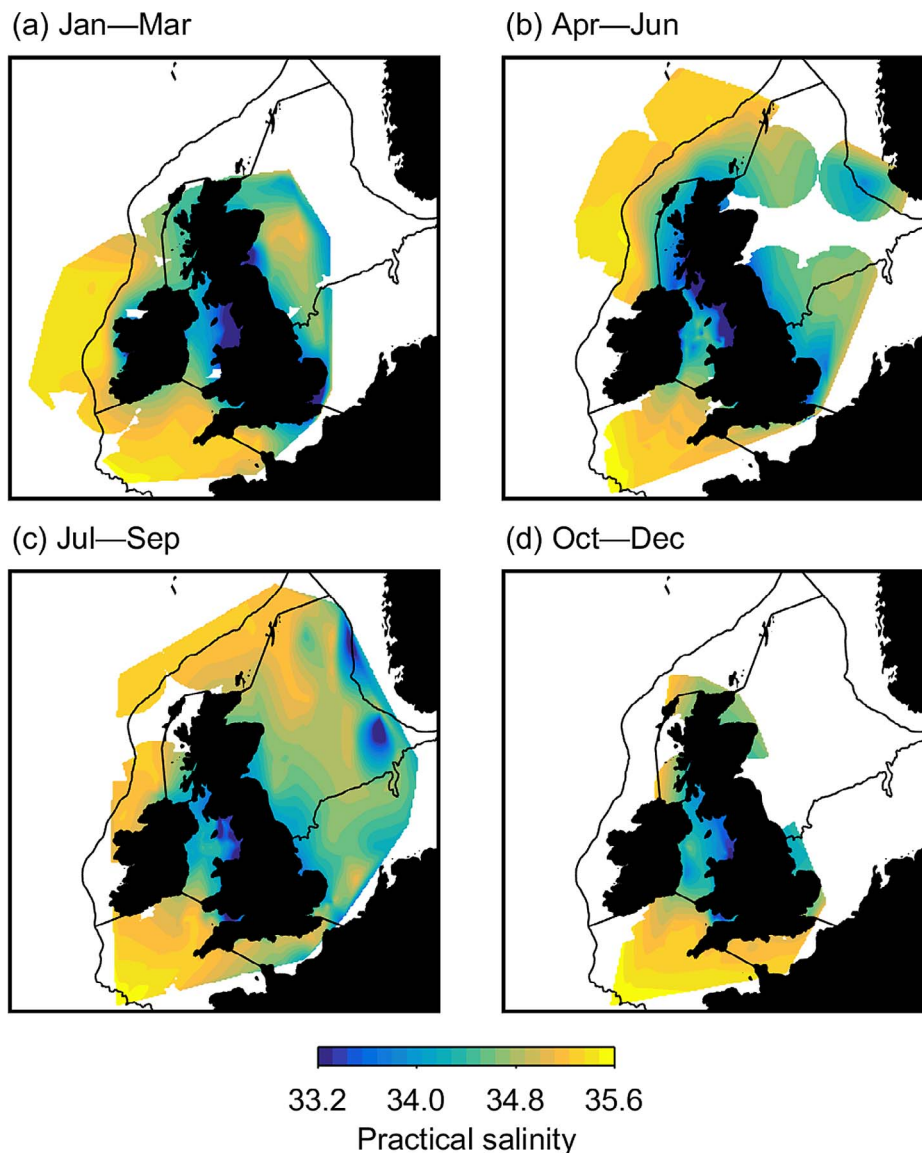


Fig. 3. Seasonal maps of sea surface salinity (SSS) as practical salinity, using sensor data taken at the point of sampling on the SSB surveys.

northern North Sea (average  $0.5 \mu\text{mol kg}^{-1}$ , region 1) and the Minches ( $1.0 \mu\text{mol kg}^{-1}$ , region 6) but remained relatively high offshore to the north of Scotland ( $6.7 \mu\text{mol kg}^{-1}$ , region 8) and in the Irish Sea ( $3.9 \mu\text{mol kg}^{-1}$ , region 5). By summer, nitrate concentrations were depleted in most regions (Figs. 4 and 5). However in Liverpool Bay (in region 5), nutrient concentrations were never fully depleted although the largest seasonal changes were observed here, with a winter to summer decrease of  $8 \mu\text{mol kg}^{-1}$  for nitrate and  $5 \mu\text{mol kg}^{-1}$  for silicate (see also Tables 1a and 1b). On the Scottish continental shelf (region 7), to the northeast of Scotland, nitrate concentrations also remained above detection (average  $1.2 \mu\text{mol kg}^{-1}$ ) into summer. In the autumn, nutrient concentrations had started to increase in Liverpool Bay (in region 5), earlier than in other regions (Figs. 4 and 5).

Phosphate concentrations were measured but have not been mapped here as they were uniform around the whole of the UK shelf (with a winter mean of  $0.55 \mu\text{mol kg}^{-1}$ , Table 1a), although some deviations in the ratio of nitrate to phosphate are discussed in Section 4.1.

### 3.2.2. Total alkalinity

Fig. 6 shows the seasonal and regional TA distribution. The annual mean TA for the whole dataset was  $2320 \mu\text{mol kg}^{-1}$ . There was a relatively large range of values, especially in the northern North Sea

(region 1), where the seasonal mean TA increased from  $2275 \mu\text{mol kg}^{-1}$  in spring to  $2310 \mu\text{mol kg}^{-1}$  in winter (Table 1b). In the high salinity Atlantic waters of the northwest approaches (region 8), seasonal mean TA values were relatively high (above  $2330 \mu\text{mol kg}^{-1}$ ) and the seasonal range was small (Table 1b). Overall, TA distribution was generally similar to salinity with higher TA offshore throughout the year and the lowest values on the shelf.

### 3.2.3. Dissolved inorganic carbon

Fig. 7 shows the seasonal and regional distribution of DIC. The largest seasonal change in DIC was in the northern North Sea (region 1) where there was over  $100 \mu\text{mol kg}^{-1}$  decrease in the seasonal mean DIC from winter to spring (Fig. 7, Table 1b). The lowest DIC concentrations observed were in spring in the northern North Sea ( $2034 \mu\text{mol kg}^{-1}$ , region 1) and the Minches (region 6, around  $2065 \mu\text{mol kg}^{-1}$ ) and in summer on the continental shelf (region 7, around  $2097 \mu\text{mol kg}^{-1}$ , Table 1b). DIC concentrations peaked in winter and decreased in the spring and summer in all regions (Table 1b), therefore DIC showed a similar distribution to nutrient concentrations.

### 3.2.4. Partial pressure of carbon dioxide

Fig. 8 shows the seasonal and regional variations in measured and

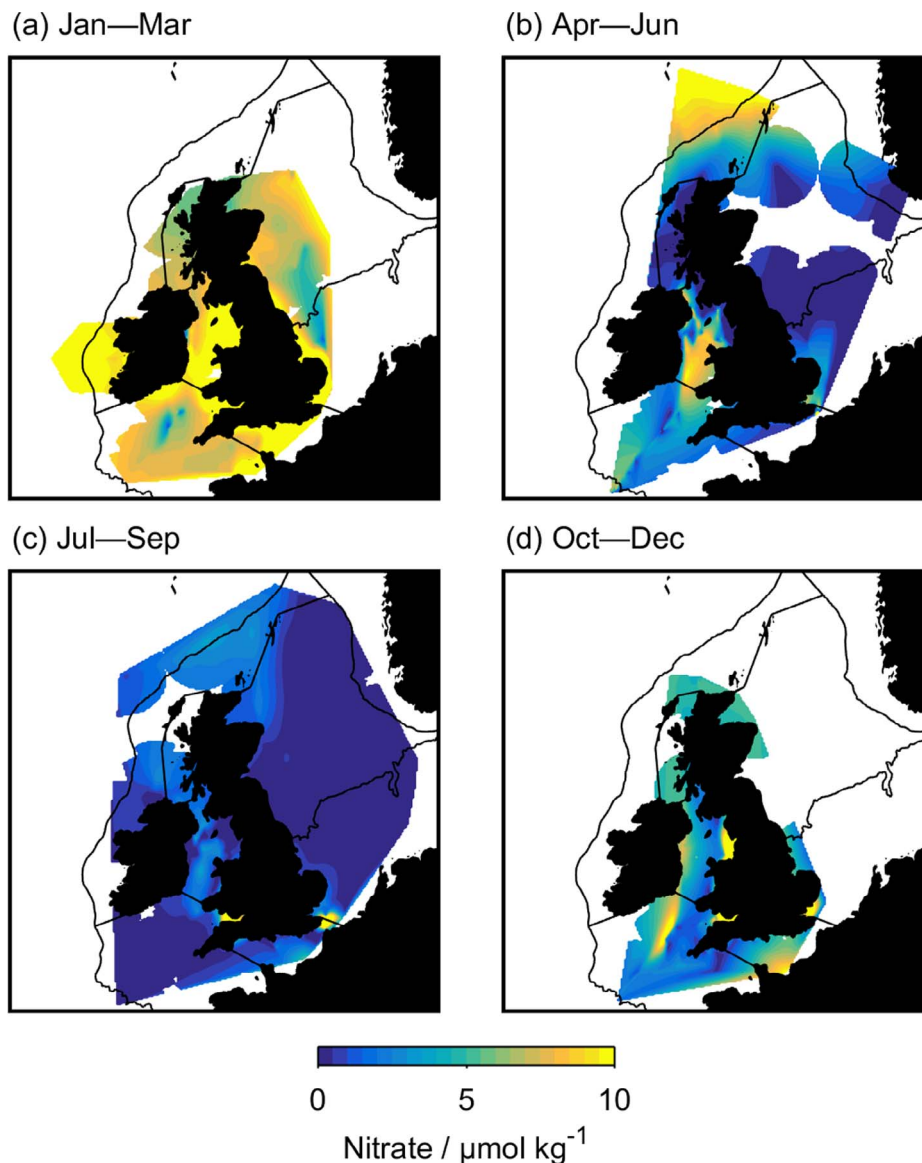


Fig. 4. Seasonal maps of sea surface nitrate concentrations, from SSB bottle samples.

calculated  $p\text{CO}_2$ . Taking an atmospheric  $p\text{CO}_2$  of 400  $\mu\text{atm}$  (Humphreys et al., 2018) then under-saturated values (relative to atmospheric  $p\text{CO}_2$ ) are indicated by the blue colours and over-saturated by the warmer colours in Fig. 8. Generally, the highest values were seen in the autumn and the lowest values for each region were in the spring (Fig. 8).

In the seasonally stratified northern North Sea (region 1)  $p\text{CO}_2$  values were generally under-saturated from winter (352  $\mu\text{atm}$ , Table 1b) to summer. However, there is some variation within this region where relatively oversaturated values were observed close to the Scottish coast from autumn to winter (Fig. 8). The largest seasonal variation in  $p\text{CO}_2$  was observed in the southern North Sea, (region 2) with an increase of over 100  $\mu\text{atm}$  between the spring and autumn (Fig. 8, Table 1b).

A seasonal over-saturation in  $\text{CO}_2$  was especially prominent in the relatively shallow inner shelf regions in summer and autumn (Fig. 8 and Table 1b). For example, a marked increase in  $p\text{CO}_2$  from spring to summer was observed in the relatively shallow eastern English Channel (region 3, from 333 to 452  $\mu\text{atm}$ , Table 1b).

In the Celtic Sea (region 4)  $p\text{CO}_2$  was predominantly under-saturated throughout the year (Fig. 8). However,  $p\text{CO}_2$  increased near to the coast in autumn when the average was 407  $\mu\text{atm}$  (Table 1b). In

contrast, the relatively shallow Irish Sea (region 5) showed a general year round over-saturation in  $p\text{CO}_2$  (with seasonal averages above 409  $\mu\text{atm}$ , Table 1b) except for in spring.

### 3.2.5. Calculated pH

Fig. 9 shows the seasonal and regional variation in calculated pH around the shelf. It is important to note that the colour scale is reversed in Fig. 9 for easier comparisons with  $p\text{CO}_2$  as an inverse relationship is expected. Overall, calculated pH was lowest around the coast in autumn and the highest calculated pH was observed in spring (Fig. 9). For example in the northern North Sea (region 1) the seasonal mean pH in spring was 8.19 when  $p\text{CO}_2$  was low (see Table 1b). In the southern North Sea (region 2) there was a spring to summer decrease in the calculated pH (from 8.15 to 8.05, Table 1b). Likewise, in the eastern Channel (region 3) the pH decreased to a similar extent from spring to summer (Table 1b). In the Irish Sea (region 5) and the Minches (region 6) the seasonal mean pH was lowest in winter (when  $p\text{CO}_2$  was high) and increased in the spring (from 8.06 to 8.18 in region 6, Table 1b).

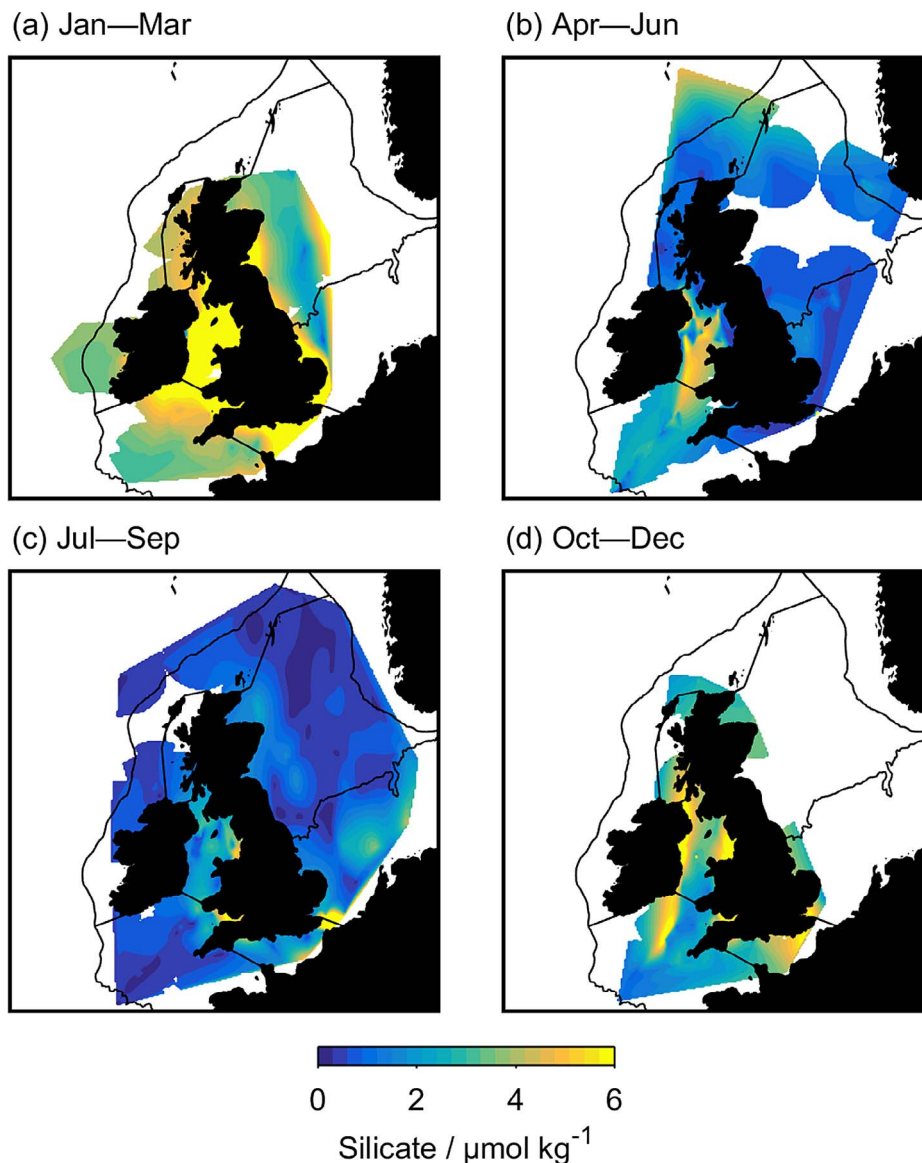


Fig. 5. Seasonal maps of silicate concentrations, from SSB bottle samples.

## 4. Discussion

### 4.1. An overview of seasonal variations in relation to regions

Dividing the UK-SSB dataset into 9 ecohydrodynamic regions revealed large regional variations in carbonate chemistry parameters in relation to nutrients and hydrography. Fig. 10 illustrates the relationship between hydrography (SST) and surface nutrient concentrations for each of the regions considered.

Overall, there was a winter peak in nutrient concentrations, then a rapid decrease in the spring and summer months. The rapid depletion in nitrate (and DIC) concentrations in spring are likely to result from their assimilation in the production of organic material by phytoplankton, during the ‘spring bloom’ (Frigstad et al., 2015). The dominant pattern on the shelf was for low nitrate concentrations throughout the spring to summer months, in warming water. Then, in the autumn months there was an increase in nitrate concentrations (as the water cools), observed in all regions where data were available (Fig. 10). The increase in nitrate concentrations during autumn months is likely to be due to the remineralisation of organic matter, the break down the thermal stratification of the surface waters and the onset of vertical mixing. This

seasonal variability is as expected at temperate latitudes (Smith et al., 2014) and gives a triangular distribution to the data points (Fig. 10). Similar patterns would be expected for DIC, especially in winter months when seasonal stratification breaks down and nitrate plus DIC accumulates in the surface waters.

The winter peak in nutrient (and DIC) concentrations are also likely due to organic matter remineralisation and the convective mixing of colder high nutrient and DIC rich waters from below (Körtzinger et al., 2008). Maximum concentrations were reached just before the return of stratification in spring in all regions (Fig. 10). However, in the Northern North Sea the autumn SST is relatively cold and associated with higher nitrate concentrations compared with other regions (Fig. 10). The relationship between SST and nitrate concentrations is less clear in the Southern North Sea (region 2, Fig. 10). Relatively low salinities were observed in the east of the southern North Sea in summer (region 2, in Fig. 3) due to fresh water entering the North Sea from the major European continental rivers (such as the Rhine). Therefore, riverine inputs are likely to have contributed to the higher nitrate concentrations seen in this region.

In the well mixed eastern English Channel (region 3) there was a pronounced ‘triangular’ shape in the relative nitrate and SST variability



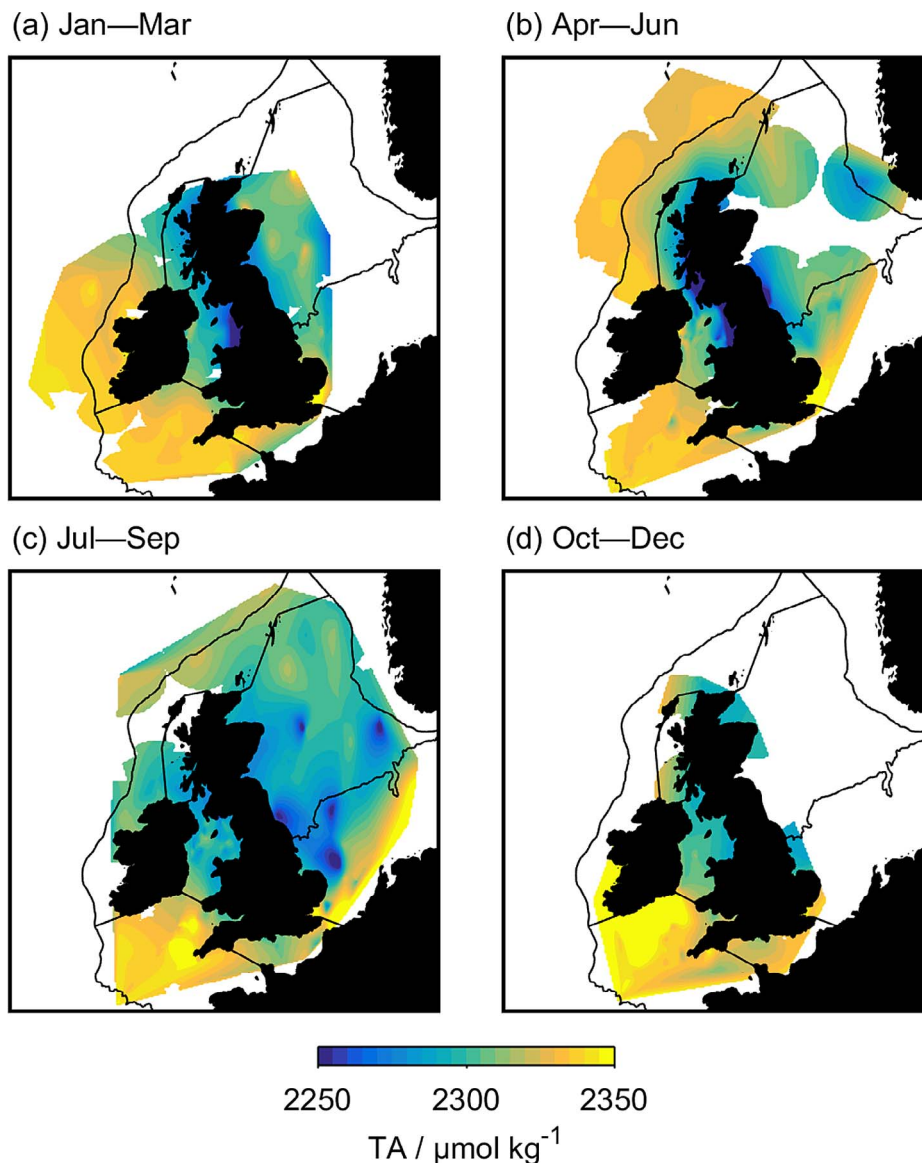


Fig. 6. Seasonal maps of total alkalinity (TA) measurements, from SSB bottle samples.

(Fig. 10). The nitrate concentrations increased earlier in the year (compared with other regions), starting in the summer whilst SST was still relatively high. This may be due to the continuous injection of nutrients into the euphotic zone that is seen in many well mixed systems (L'Helguen et al., 1996). High nitrate (and silicate, Fig. 5) concentrations were observed for most of the year in the eastern Channel (region 3), probably from the remineralisation of organic material in these relatively shallow and well-mixed regions.

In the western English Channel and the Celtic Sea (region 4), an area characterised by seasonal thermal stratification (Smyth et al., 2010; Smith et al., 2014), the highest nitrate concentrations were generally observed in the winter (Fig. 10, from January to March). In the central Irish Sea (region 5) nitrate was never depleted, even during spring and summer, possibly due to riverine inputs (Greenwood et al., 2011). The seasonal mean salinity remained relatively low ( $\sim 33.9$ , Table 1a) throughout the year in the Irish Sea and Liverpool Bay (region 5) showing a high influence of fresh water input to the region (Hydes and Hartman, 2012; Greenwood et al., 2011). Silicate concentrations in the Irish Sea (region 5) were at least  $1 \mu\text{mol kg}^{-1}$  higher than other regions throughout the year (Fig. 5), probably due to this riverine influence. Seasonal coverage is relatively poor for the Minches (region 6) and the

Norwegian trench (region 9), as seen in Fig. 10.

In the more open ocean continental shelf (region 7) and Atlantic northwest approaches (region 8) there was a linear relationship between nitrate and temperature, likely due to the spring nitrate depletion and autumn nitrate regeneration (Fig. 10). To the far north of Scotland (in region 7) nitrate concentrations remained high ( $> 5 \mu\text{mol kg}^{-1}$ ) until the summer months (Fig. 10), probably due to the general northward delay in bloom timing (Siegel et al., 2002). From the linear relationship seen in Fig. 10 the nitrate concentrations could almost be predicted from SST, as shown by Sathyendranath et al. (2001); Henson et al. (2003).

#### 4.2. Stoichiometry

Fig. 11(a–c) shows the relationship between nitrate and phosphate. These figures confirm the similarity in spatial distributions between nitrate and phosphate, although most of the values were below the open ocean 'Redfield' stoichiometric ratio of 16:1 (Redfield et al., 1963; Anderson and Sarmiento, 1994). In the present study, some especially low nitrate values, relative to phosphate concentrations, were seen in both the southern North Sea (region 2, Fig. 11a) and the Irish Sea

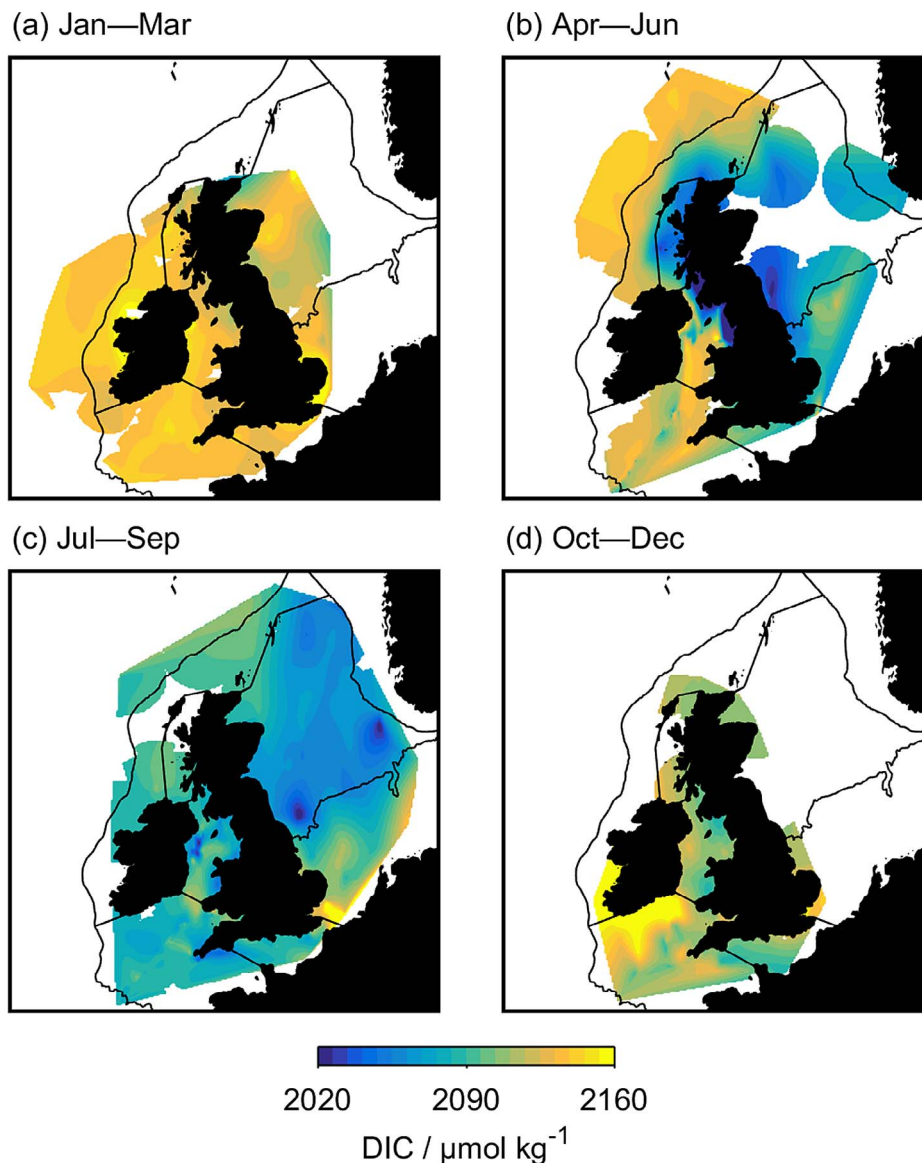


Fig. 7. Dissolved Inorganic Carbon (DIC) measurements, from SSB bottle samples.

(region 5, Fig. 11b). Likewise there is a relatively low N:P in the Celtic Sea (region 4, Fig. 11b). The N:P relationship approaches the 16:1 (Anderson and Sarmiento, 1994) ratio in the more Atlantic influenced off shelf areas (regions 6–8, Fig. 11c).

Nutrient concentrations are likely to be higher near the coast than in the open ocean, particularly where there are riverine inputs. However, a key feature established in the North Sea Project data (Hydes et al., 1999) was that the maximum nitrate concentrations observed in the Central North Sea (Hydes et al., 1999) and in the Irish Sea (Gowen et al., 2002, 2008) were below those observed in ocean waters adjacent to the shelf (Hydes et al., 2004). This resulted in low nitrate to phosphate (N:P) ratios (Hydes et al., 1999; Gowen et al., 2002), probably from denitrification in the sediments of these relatively shallow (and well mixed) seas (Setzinger and Giblin, 1996). Recently Kitidis et al. (2017) also showed that sediment anaerobic ammonium oxidation and denitrification removed 6–9% of the nitrate in the Celtic Sea over an annual cycle.

Fig. 11(d–f) shows the relationship between DIC and nitrate. Overall, there was a positive correlation between DIC and nitrate around the northwest European Shelf. However there was large variability in this relationship within and between the regions. For example

in the northern North Sea (region 1) most points were above the line shown in Fig. 11d (that represents the open ocean C:N of 7.3, Anderson and Sarmiento, 1994). In the southern North Sea (region 2) there was a pronounced variability in the C:N relationship at very low nitrate concentrations (Fig. 11d). In the Celtic Sea (region 4) there was a variation in the C:N ratio as the nutrient concentration increased (Fig. 11e). However, on the Irish and Scottish shelf (region 7) most of the points followed this line (Fig. 11f).

A positive correlation was generally observed between DIC and nitrate, as both are influenced by productivity and the breakdown of organic material. Where the variability in the C:N relationship was pronounced at very low nitrate concentrations, for example in the southern North Sea (region 2), this may be a further indication of denitrification. This process is significant in the North Sea (Hydes et al., 1999) and could contribute to the relatively low nitrate values observed in both the N:P and C:N ratios (Fig. 11) in this region. However, riverine input can be an additional source of variability in the C:N relationship in the more coastal systems through both nutrient input (Greenwood et al., 2011) and DIC input (McGrath et al., 2016).

In the Celtic sea (region 4), the points were above the line at low nitrate concentrations and below the line at higher concentrations

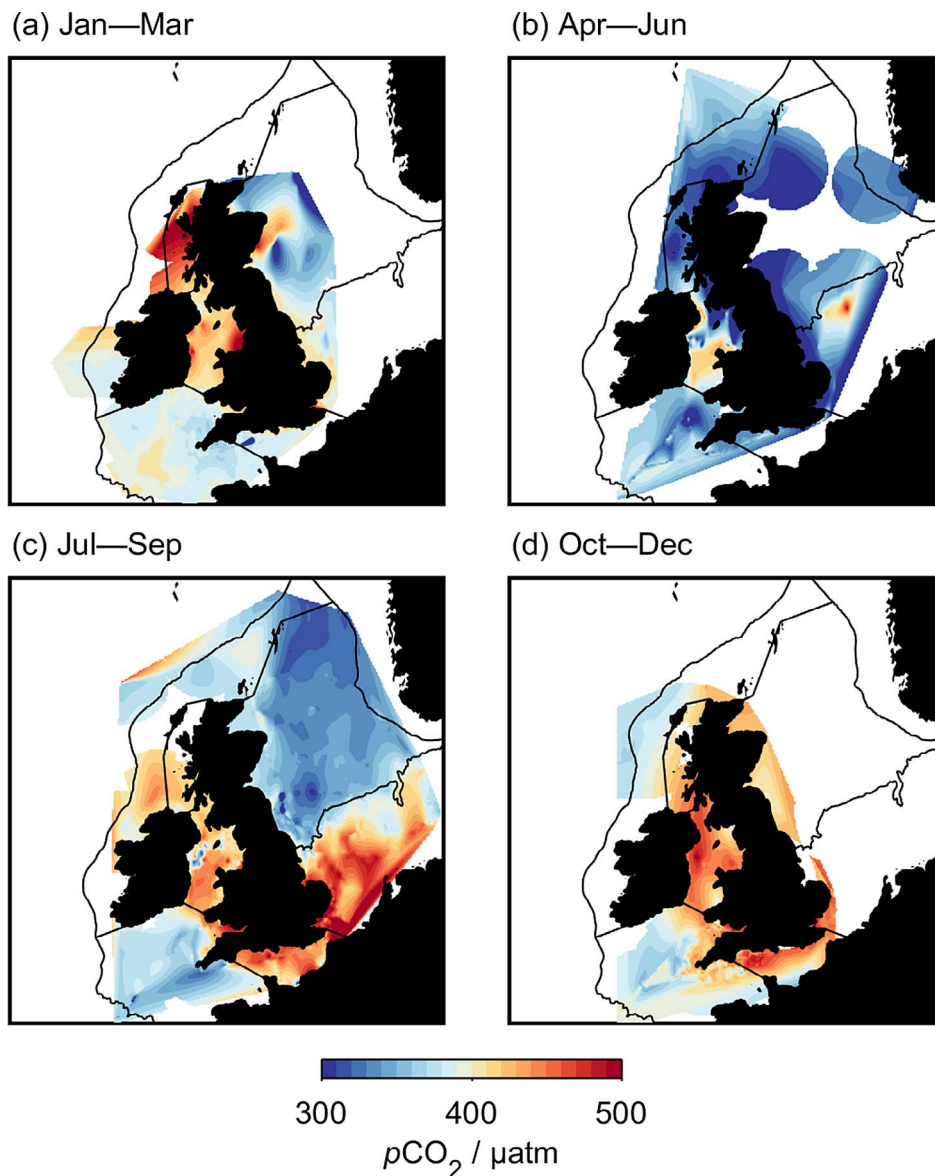


Fig. 8. Surface  $p\text{CO}_2$ , calculated from bottle samples analysed for DIC/TA (using  $\text{CO}_2\text{SYS}$ ) and measured  $p\text{CO}_2$  from underway systems on the RRS *Discovery* and RV *Cefas Endeavour* (2014–2015).

(>  $8 \mu\text{mol kg}^{-1}$ , Fig. 11e). So, the C:N ratio was initially high in the potentially productive periods (periods of productivity were identified for the Celtic Sea by Hickman et al., this issue), when nitrate concentrations were lower. Then the C:N decreased at high nitrate concentrations. High C:N suggests a more efficient recycling of nitrate compared with carbon and that the organic material exported from the surface would be carbon enriched (Sambrotto et al., 1993). Therefore spatial and seasonal changes in C:N could have a significant impact on carbon cycling and export off the shelf via the continental shelf pump (Gruber and Galloway, 2008; Painter et al., 2017). Variation in the C:N will also have implications for methods that calculate productivity from the depletion in DIC or nitrate (Frigstad et al., 2015 and references therein) using the ‘standard’ C:N Redfield ratio of 6.6:1 (Anderson and Sarmiento, 1994).

#### 4.3. Controls on seawater $p\text{CO}_2$

The solubility of  $\text{CO}_2$  depends mainly on temperature (increased solubility at low temperature, decreased at high temperatures). In turn, biological production processes tend to decrease surface water  $p\text{CO}_2$ ,

whereas respiration and remineralisation processes tend to increase surface water  $p\text{CO}_2$  (Shadwick et al., 2011). The dominance of these processes varies through the year and with region (Takahashi et al., 2002; Jiang et al., 2013). To study this further we assessed the physical and biological forcing on  $p\text{CO}_2$ . Fig. 12 shows the thermal component of the change in  $p\text{CO}_2$  calculated following Takahashi et al. (2002). Fig. 13 shows the residual between the total and thermal component of change and represents the non-thermal component, which we assume to be largely biologically driven. This is either through the remineralisation of organic matter in the surface layer, or the addition of remineralised nutrients from the deep layer through vertical mixing. The magnitude of this component may be reduced by any air-sea gas exchange.

Our study showed the dominance of thermal control (Fig. 12) on the  $p\text{CO}_2$  especially in the spring and summer. Temperature can be the main factor influencing the  $p\text{CO}_2$  variability, through the control on stratification and stabilisation of the water column triggering production.

The spring time decrease in  $p\text{CO}_2$ , to under saturated levels was seen in all regions and coincided with a large decrease in nutrients in

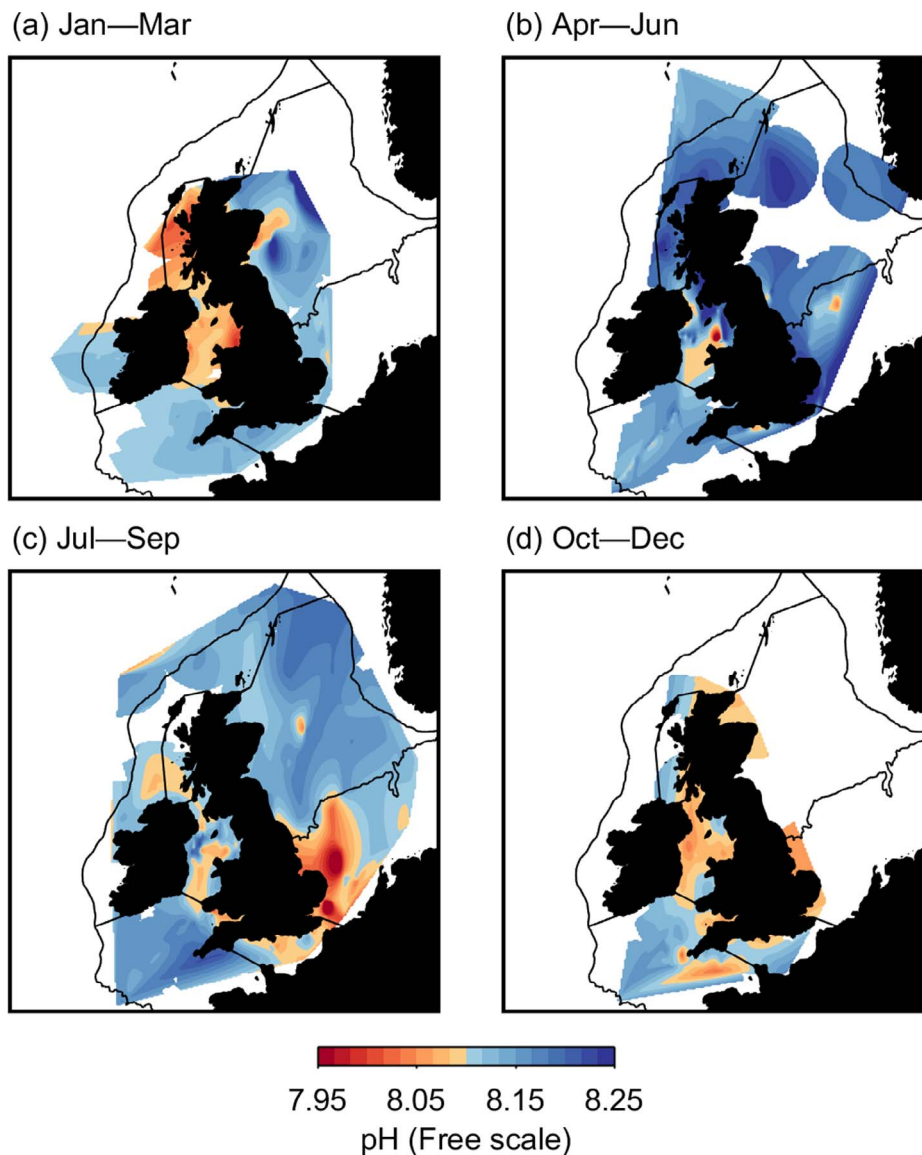


Fig. 9. pH (freescale), calculated from bottle samples analysed for DIC/TA (using CO<sub>2</sub>SYS).

these productive waters (Table 1), as shown by Thomas et al., (2005). Biological production can impact surface pCO<sub>2</sub> in summer in stratified systems by the presence of subsurface phytoplankton blooms below the (shallow) thermocline (Shadwick et al., 2011). Non-thermal or biological control dominated from autumn through to winter (Fig. 13) due largely to regeneration from the respiration of organic material.

There were clear regional variations in the balance of thermal and non-thermal controls. For example in the central region of the northern North Sea (region 1) there was a thermally driven increase in pCO<sub>2</sub> of about 70  $\mu$ atm from winter to spring (Fig. 12), and a non-thermal decrease of 110  $\mu$ atm (Fig. 13). This region seasonally stratifies and DIC is transported off shelf (Huthnance et al., 2009). Overall, in the seasonally stratified northern North Sea (region 1), the control of pCO<sub>2</sub> was predominantly non-thermal (biological, as shown in Fig. 13), as has been shown previously (Thomas et al., 2005; 2006; Van Leeuwen et al., 2015). In contrast, in the well-mixed, shallower southern North Sea (region 2) thermal controls on pCO<sub>2</sub> dominated (Fig. 12). In this region, water temperature was the dominant control on both pCO<sub>2</sub> and nutrient concentrations (Thomas et al., 2005, 2006; Van Leeuwen et al., 2015).

Our study suggested that the eastern English Channel (region 3) was over-saturated in CO<sub>2</sub> in the autumn (Fig. 8). This was when non-thermal heterotrophic processes, such as organic matter

rem mineralisation, dominated (Fig. 13). An autumnal over-saturation of CO<sub>2</sub> has been observed previously in the eastern English Channel (Frankignoulle et al., 1996; Jiang et al., 2013). Borges (2005) also suggested that the permanently well-mixed and shallow ecosystems within the eastern English Channel were seasonally over-saturated and a seasonal source of CO<sub>2</sub>.

Overall pCO<sub>2</sub> in the Celtic Sea (region 4) was close to the atmospheric pCO<sub>2</sub> for most of the year (Fig. 8), with a pronounced under-saturation in spring (to a mean average of 364  $\mu$ atm, Table 1). This is similar to the observations made by Kitidis et al., (2012). The seasonal variations in pCO<sub>2</sub> were dominated by biology rather than advection in the northern part of the western English Channel (Fig. 13). In contrast, the data suggested that in the Irish Sea (region 5) pCO<sub>2</sub> was over-saturated for most of the year (Fig. 8). There was a dominance of non-thermal controls on pCO<sub>2</sub> in autumn and winter in the Irish Sea (region 5), and the non-thermal influences were especially high near to the coast (Fig. 13). pCO<sub>2</sub> remained higher here than if it were in equilibrium with the atmosphere for most of the year (Table 1), except for in the spring when there was a pronounced under-saturation in the surface waters.

In the Minches (region 6), the non-thermal component was especially high in winter and had little influence for the rest of the year. In



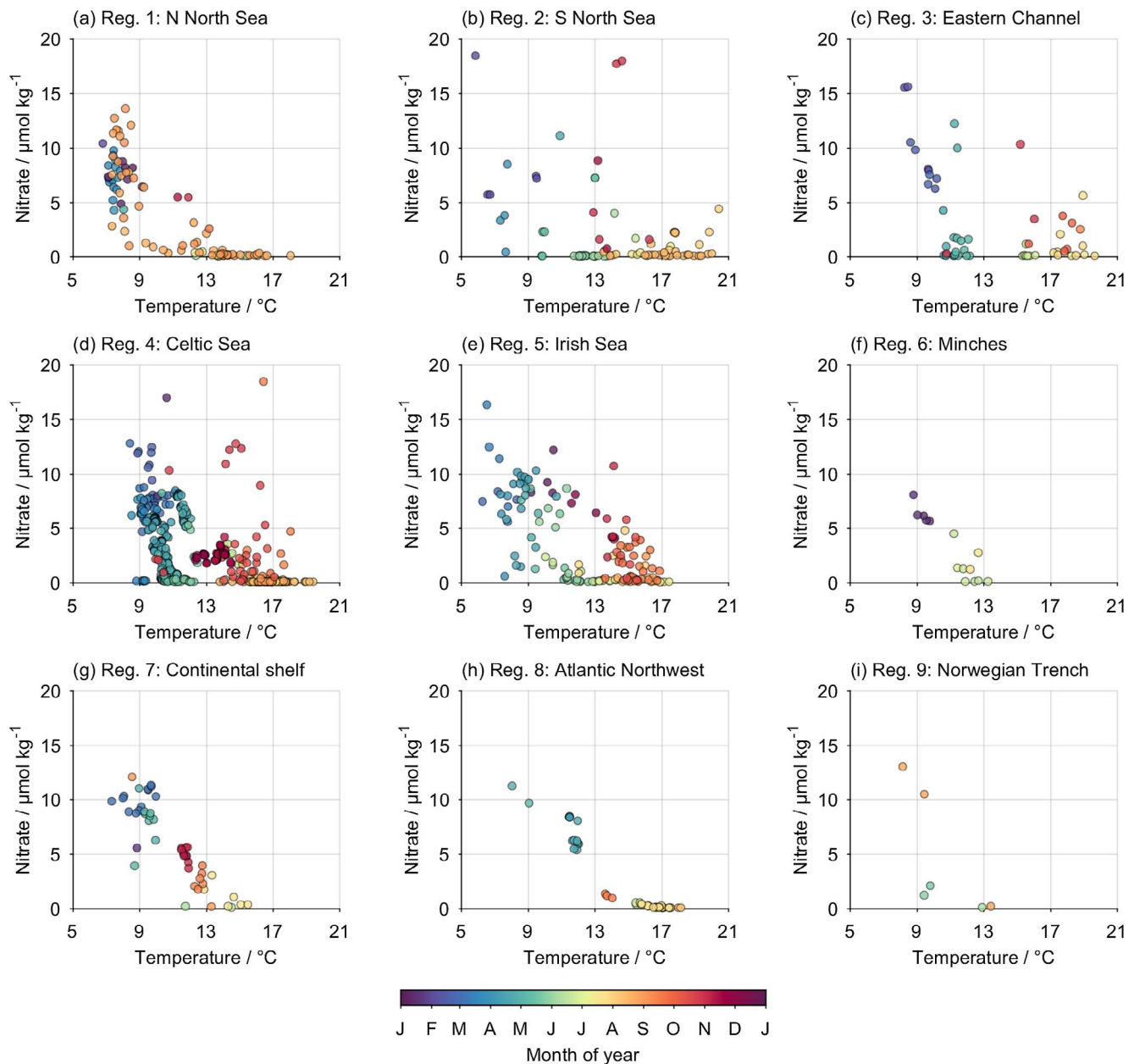


Fig. 10. Measured nitrate concentrations and sea surface temperature for each month and region.

the wider sub-polar Atlantic, the seasonal cycle of  $p\text{CO}_2$  was dominated by the mixing of cold water (leading to increased  $\text{CO}_2$  solubility). This was seen to the west of Ireland (region 7) where both the thermal and non-thermal components increased  $p\text{CO}_2$  in the autumn and winter.

In summary, the largest thermal component observed was in the summer to the south of the UK (Fig. 12), especially in the southern North Sea (region 2) and the eastern English Channel (region 3) where the highest SST had been observed in summer (Fig. 2). The largest non-thermal component observed (Fig. 13) was in winter, especially around the coast in Liverpool Bay (region 5) and the Minches (region 6). In all of these well-mixed and shallower regions, it is likely that the decaying bloom, and breakdown of organic material (Thomas et al., 2005), increased the  $p\text{CO}_2$  in autumn and winter. As these regions remain mixed the  $p\text{CO}_2$  super-saturation persists until the next spring.

Our seawater  $p\text{CO}_2$  data has been used to assess potential sources and sinks around the shelf (Kitidis et al., 2018 in prep.). The direction of air-sea gas fluxes are driven by concentration differences between the seawater and atmosphere. Where  $p\text{CO}_2$  in seawater was under-

saturated compared with the atmospheric  $p\text{CO}_2$  it suggests that this area will be a sink; if it exceeded  $p\text{CO}_2$  in air then this suggests the region will be a source to the atmosphere. However, the magnitude of the flux is modulated by other processes, for which wind speed can be used as a proxy (Wanninkhof, 2014). This is explored further in Kitidis et al. (2018, in prep.) and the NW European shelf was found to be net autotrophic and a  $\text{CO}_2$  sink over the period of our study.

The separation into ecohydrodynamic regions (after Bresnan et al., 2015) was done to distinguish the different hydrographical regions. These separations correspond well to the biogeochemical variability observed from the data. However, if you go further into the details then more complex and dynamic hydrographical systems are observed, such as tidal fronts between the year round well-mixed and seasonally stratified ecosystems, shelf break systems and estuarine systems. The on-shelf tidal frontal zones between the permanently well-mixed and seasonally stratified areas are particularly productive and can influence  $\text{CO}_2$  exchange and examples of these frontal regions are seen in the Irish Sea (Simpson and Hunter, 1974) and in the Celtic Sea (Pingree and

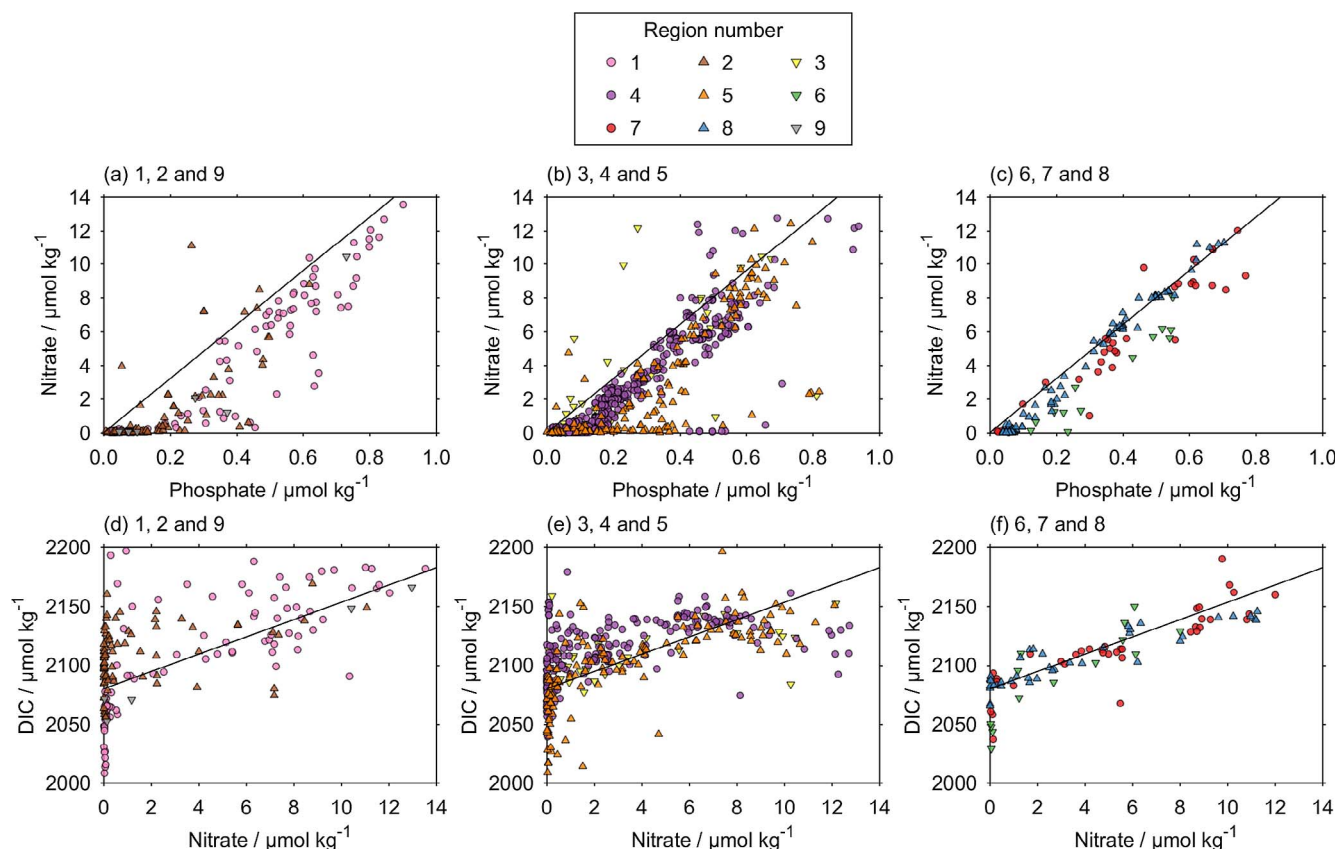


Fig. 11. A comparison of the (a–c) nitrate and phosphate concentrations (in groups of 3 regions for ease of viewing) showing the Anderson and Sarmiento (1994) N:P ratio of 16:1 as a solid line and (d–f) the relationship between DIC and nitrate with the C:N ratio of 7.3 as a solid line (Anderson and Sarmiento, 1994).

Griffiths, 1978). For example within the seasonally stratified Celtic Sea (region 4) the southern part of the western English Channel and the waters around Land's End (Marrec et al., 2013), can be distinguished in the hydrography. Within the western Channel and Celtic Sea (region 4) there was a clear division between the northern sub-region, where there was a dominance of non-thermal control of  $p\text{CO}_2$  in winter and the southern part where thermal effects dominated (Fig. 12).

#### 4.4. Changes in alkalinity and pH

The TA and salinity distribution is generally similar as both are strongly influenced by evaporation, riverine freshwater inputs and precipitation. TA can be considered as conservative in the open ocean where TA and salinity tend to be linearly related (Lee et al., 2006; Jiang et al., 2014). Near coastal waters, with a strong salinity gradient, are ideal places to get a TA: S linear relationship. However in the current study the real near coastal water area was not assessed, and it was difficult to get see a linear TA:S relationship in such diverse ecosystems although the low salinity water was generally associated with low TA values. The offshore increase in salinity (Fig. 3) and TA (Fig. 6) dominated over any seasonal variations.

Many processes result in a TA increase in near coastal waters (Cai et al., 2011; Thomas et al., 2007), such as the increase in TA by the oxidation of organic material in marine sediments (Froelich et al., 1979). The southern North Sea (region 2) and the eastern Channel (region 3) both showed large variability in TA compared with other regions as these shallow areas are influenced by high organic material (Salt et al., 2016). Coastal regions are also influenced by riverine input, where the presence of calcareous limestone bedrock can increase TA in shelf waters. For example, the high TA river Liffey near Dublin inputs to the Irish Sea (region 5) although in this case the effects will only be observed near to the coast due to a low riverine discharge (McGrath

et al., 2016). Previous studies have shown some seasonality in TA due to productivity, for example Hydes and Hartman (2012) showed higher TA during the spring bloom in the Liverpool Bay sub-region of the Irish Sea (region 5). On the northwest European shelf large coccolithophore blooms can also strongly influence alkalinity and calcification will affect the TA and seawater  $p\text{CO}_2$  (Harlay et al., 2010).

In the present study, large seasonal variations in pH were observed around the shelf, (up to 0.2 units, Table 1b). The pH range is influenced by DIC, TA and changes in temperature and by the balance between photosynthesis and respiration. There is generally an inverse relationship between  $p\text{CO}_2$  and pH, due to the increase in  $\text{H}^+$  ions (i.e. decreased pH) when  $\text{CO}_2$  dissolves in seawater (Zeebe and Wolf-Gladrow, 2001). pH increased in spring in all regions (Table 1b) when photosynthesis dominated over respiration. pH then decreased in summer in most regions (Table 1b): for example in the Southern North Sea (region 2) pH decreased from spring to summer (8.15 to 8.05, Table 1), as respiration became more important (Provoost et al., 2010). Previous studies found similar large seasonal variations in pH (up to 0.3) especially off the east coast of Scotland, around the Stonehaven time series site (Hydes et al., 2011; Ostle et al., 2016).

In the North Sea (regions 1 and 2) and the eastern Channel (region 3), where temperature control on  $p\text{CO}_2$  dominated, there was a winter to summer increase in  $p\text{CO}_2$  (and associated pH decrease), possibly influenced by the remineralisation of organic matter in these shallower regions. The  $p\text{CO}_2$  increase (and pH decrease) at the end of summer, is likely to be due to the influence of temperature and the remineralisation of organic matter by microbial processes through the sediment–water interface in these relatively shallow regions. The process of denitrification over muddy sediments could also influence pH although we would expect a pH increase due to this process (Froelich et al., 1979; Provoost et al., 2010).

The strong pH fluctuations in shelf seas and coastal waters (Duarte

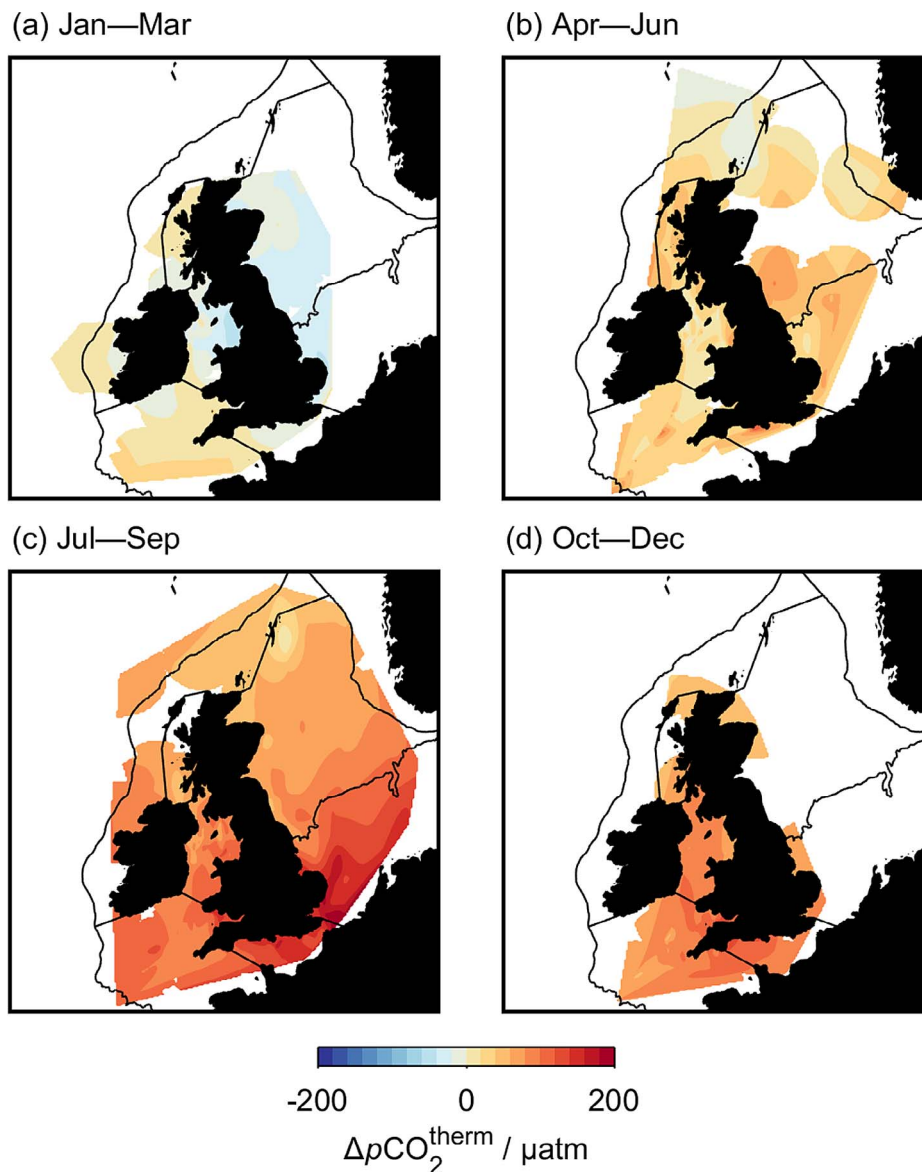


Fig. 12. The thermal component of the change in  $p\text{CO}_2$  calculated following Takahashi et al. (2002).

et al., 2013; Ostle et al., 2016; Waldbusser and Salisbury, 2014) imply that the concept of ocean acidification (OA) is difficult to transpose to coastal ecosystems, where the rates and variability of OA are higher than in the open ocean (Doney et al., 2009). The occurrence of vibrant biological communities in areas with large regional and seasonal variations in seawater pH imply that they possess an inbuilt tolerance to pH changes (Bates et al., 2014; Kitidis et al., 2017). This tolerance may occur due to the ability of seawater to buffer some of these pH changes through its alkalinity. TA will buffer the hydrogen ions so the buffering capacity of seawater is a direct function of TA as regions with high TA will be less prone to rapid changes in OA. The DIC:TA relationship for example can be strongly linked to different buffer factors (eg: Egleston et al., 2010). Studies such as ours give some indication of the present pH variability over the NW European Shelf, which will be useful in the future in the context of ocean acidification. This study also identified regions where the lowest TA values coincided with the lowest pH, such as the Southern North Sea (region 2, see Table 1). The low TA may suggest regions with a decreased capacity to buffer pH changes in the future.

Future OA could have detrimental effects on calcifying organisms (Feely et al., 2009; Riebesell and Tortell, 2011; Doney et al., 2011). In

the current study, calcite (Fig. 14) and aragonite (Fig. 15) were not generally under-saturated. Calcite saturation was always in the range of 1.5–4.8 and aragonite was virtually never under-saturated (1.0–3.1; about 0.3% of total measurements were < 1). Aragonite is the most soluble form of calcium carbonate in the marine environment and saturation will decrease as pH decreases (Feely et al., 2009), giving an indication of susceptibility of a region to ocean acidification. Low saturation coupled with low pH would affect the ability of organisms to form shells and skeletons (Fabry et al., 2008). Model data from Artioli et al., (2014) showed localised potential under-saturation of aragonite in the German Bight by the end of the 21st century. Changes in temperature,  $p\text{CO}_2$  and calcification would all further increase the vulnerability of these regions to OA in the future (Bates et al., 2014).

As the seasonal variation in pH can be large (Ostle et al., 2016) long-term time series measurements are required to detect any inter-annual trends (Bates et al., 2014). Ideally, over 25 years of consistently measured data are required to detect pH trends (Henson et al., 2016) although ICES studies in the central North Sea (Beare et al., 2013) and southern North Sea (Duarte et al., 2013) have reported a decadal decline in pH. This decline in pH was associated with physical drivers (Salt et al., 2013) and changes in nutrients and eutrophication

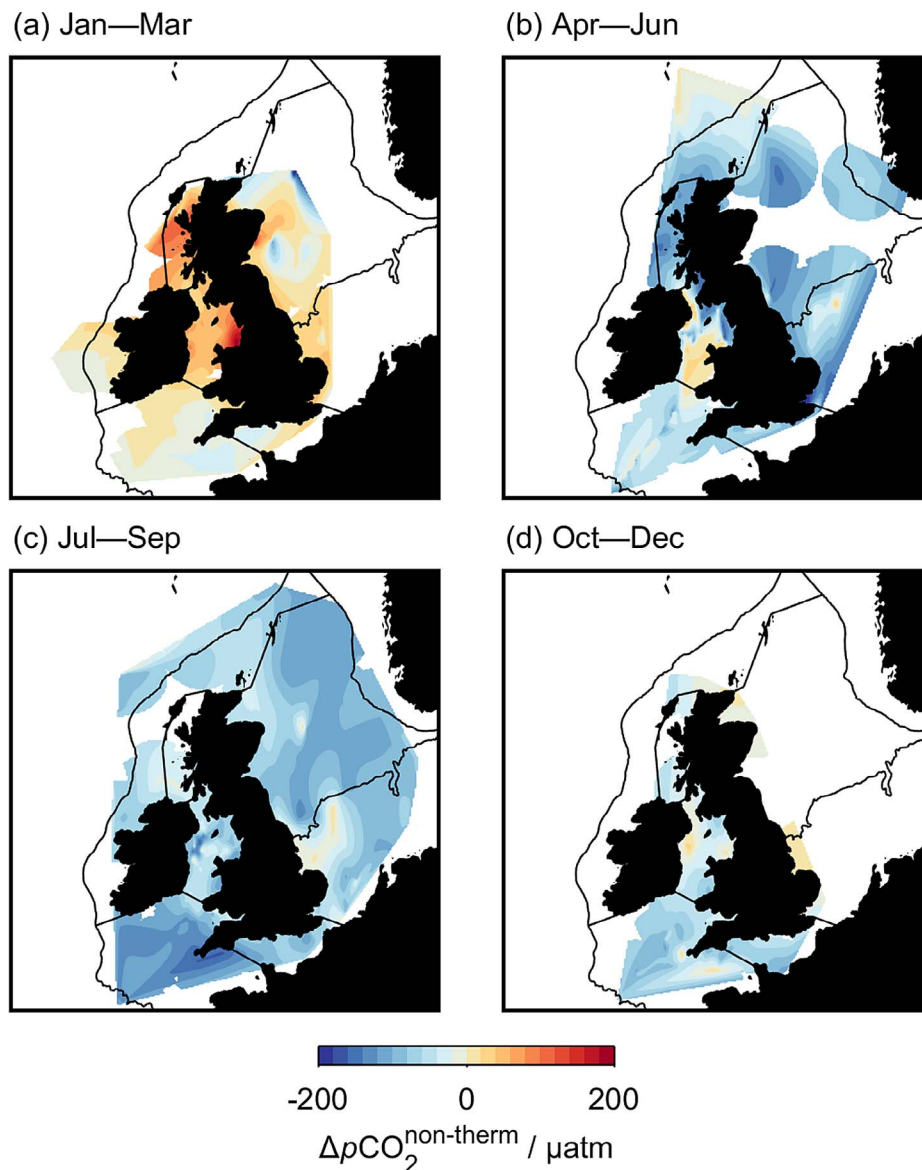


Fig. 13. The non-thermal component of the change in  $p\text{CO}_2$  (calculated following Takahashi et al., 2002 as the residual between the total and thermal component of change).

(Provoost et al., 2010). Hydes et al., (2011) showed a trend of decreasing pH around the NW European Shelf of  $-0.002$  to  $-0.004$  pH units per year between 1995 and 2009. If sample collection were to be continued around the shelf, the present study could be used to extend this emerging time series.

## 5. Conclusions

We have synthesised the spatial distributions of nutrients and carbonate chemistry around the northwest European shelf. The data were divided into 9 ecohydrodynamic regions including well-mixed inner shelf and seasonally stratified outer shelf regions. The general trends in carbon chemistry were related to changes in the hydrography and nutrients (representing biological activity and riverine input). The seasonally stratified regions, (for example off shore on the Continental slope, region 7), showed a clear inverse relationship between SST and surface nitrate (and DIC) concentrations. This was in contrast to the well mixed regions, such as the eastern channel (region 3), where the regeneration of nutrients occurred at higher temperatures. The regional variations in the DIC to nutrient relationship will have implications for calculations of carbon export.

The effects of thermal and non-thermal processes influencing  $p\text{CO}_2$  have been shown for different seasons and regions. For example in the near-shore and relatively shallow ecosystems such as the eastern English Channel (region 3) and southern North Sea (region 2) there was a thermally driven increase in  $p\text{CO}_2$  to above atmospheric levels in summer. Non-thermal processes (such as mixing and the remineralisation of organic material) dominated in winter, especially to the northwest of Scotland (region 6) and in Liverpool Bay (region 5). In all regions, the seawater  $p\text{CO}_2$  was under-saturated in spring in respect to the atmospheric equilibrium. In the well-mixed inner shelf regions  $p\text{CO}_2$  was over-saturated for the rest of the year whereas  $p\text{CO}_2$  remained under-saturated throughout the year in the seasonally stratified regions such as the Celtic sea (region 4). The seasonal variations in under and over saturation of  $p\text{CO}_2$  will have implications in calculations of shelf wide net  $\text{CO}_2$  flux, presented and discussed in Kitidis et al. (in prep., 2018). TA concentrations remained relatively constant seasonally and showed a similar distribution to salinity, as both are influenced in part by evaporation and precipitation. However, the lowest TA and lowest pH values were observed at the end of winter in the northern North Sea (region 1). We have shown that calcite saturation values are currently above 1.0 in all regions and such results will be useful for studies of ocean acidification in the future.



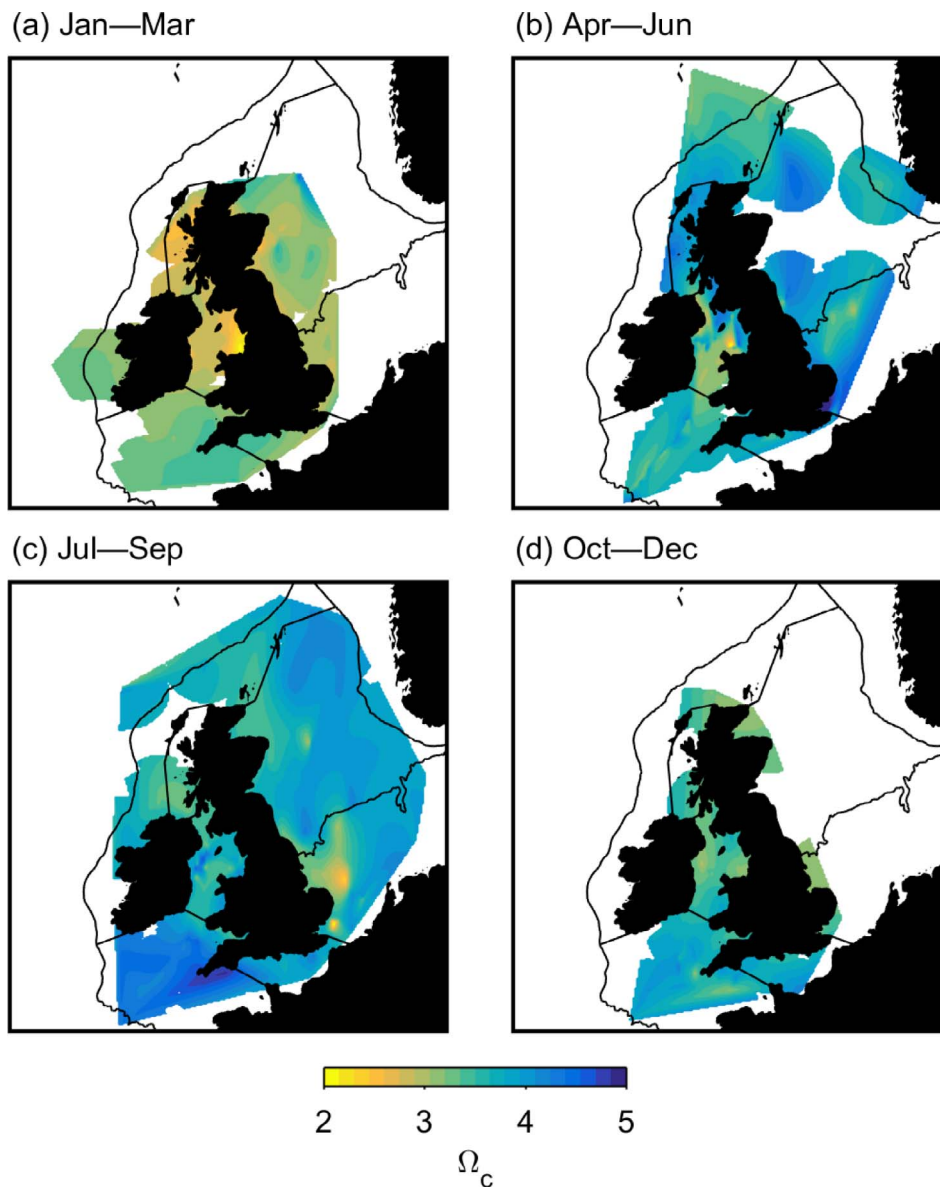


Fig. 14. Calcite saturation ( $\Omega_c$ ) calculated from SSB bottle DIC and TA.

This synthesis provided a 18 month ‘snapshot’ of the diverse and dynamic ecosystems around the northwest European shelf. It is complicated to catch the variability of complex ecosystems as the ecohydrodynamic regions studied were very diverse and dynamic. Within each region further subdivisions were identified and the seasonal variation in biogeochemistry within these regions will have implications for using such broad hydrographic divisions to study biogeochemical variations on the northwest European shelf. Incorporating high frequency underway data (as was available for  $pCO_2$  measurements) improved both the seasonal and spatial coverage over what was possible with bottle sampling alone. Generally, the wintertime period was under sampled, as were some regions year round, including the Norwegian Trench (region 9) and the Minches (region 6). Addressing these issues could be the focus for further sampling campaigns. The increased use of autonomous measurements on robust platforms (such as buoys and autonomous surface vehicles) would help in this regard.

The data have sufficient coherence and breadth of coverage to develop models that would link physical and biogeochemical processes. The SSB data set could also be used to extend existing studies to create a time series. Once we have a longer time series, we could use this data set to quantify trends in pH and  $pCO_2$ , so we recommend that the

sampling continue to quantify year-to-year variability and elucidate trends in the data. In conclusion, the large database collected as part of the shelf wide sampling within the SSB project will improve the understanding of carbonate chemistry in relation to nutrient biogeochemistry over the North-Western European Shelf, particularly in the context of climate change and ocean acidification.

#### Key message

We describe seasonal and regional variability in carbonate chemistry around the north-west European shelf, from a large and unique 1.5 year dataset of biogeochemical sampling combined with underway  $pCO_2$  data. The data has improved understanding of carbonate chemistry in relation to nutrient biogeochemistry, showing seasonal variations between the well-mixed inner shelf and seasonally stratified outer shelf regions.

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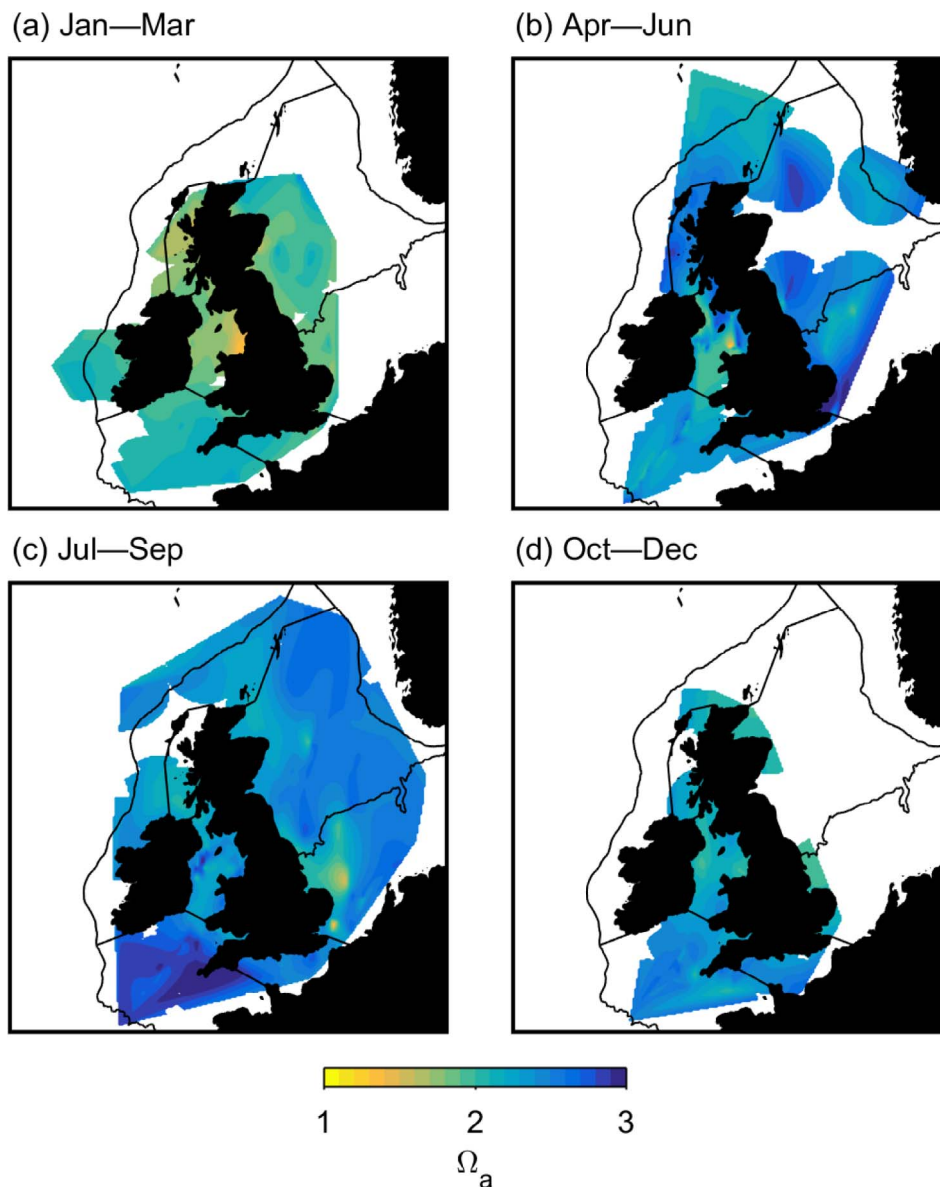


Fig. 15. Aragonite saturation ( $\Omega_a$ ) calculated from SSB bottle DIC and TA.

reference number NE/K001701/1; PML grant reference NE/K002058/1; Cefas grant number NE/K001957/1; University of Southampton reference NE/K00185X/1. We would like to thank all of our samplers and cruise participants plus the many people involved in rerouting the frozen samples as required. We are also indebted to all scientific staff, crew and officers on board the many ships and campaigns involved in this study. We are very grateful to the two anonymous reviewers who have added substantially to the interpretation. All of the SSB shelf wide sampling data are publicly available through BODC <http://www.uk-ssb.org/data/> and as listed in the references.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.pocean.2018.02.005>.

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